顔料等化成品中の副生PCB

中野　武

（大阪大学　環境安全研究管理センター）

PCB CONGENER PROFILE OF UNINTENTIONAL FORMATION FROM PIGMENT MANUFACTURING PROCESS

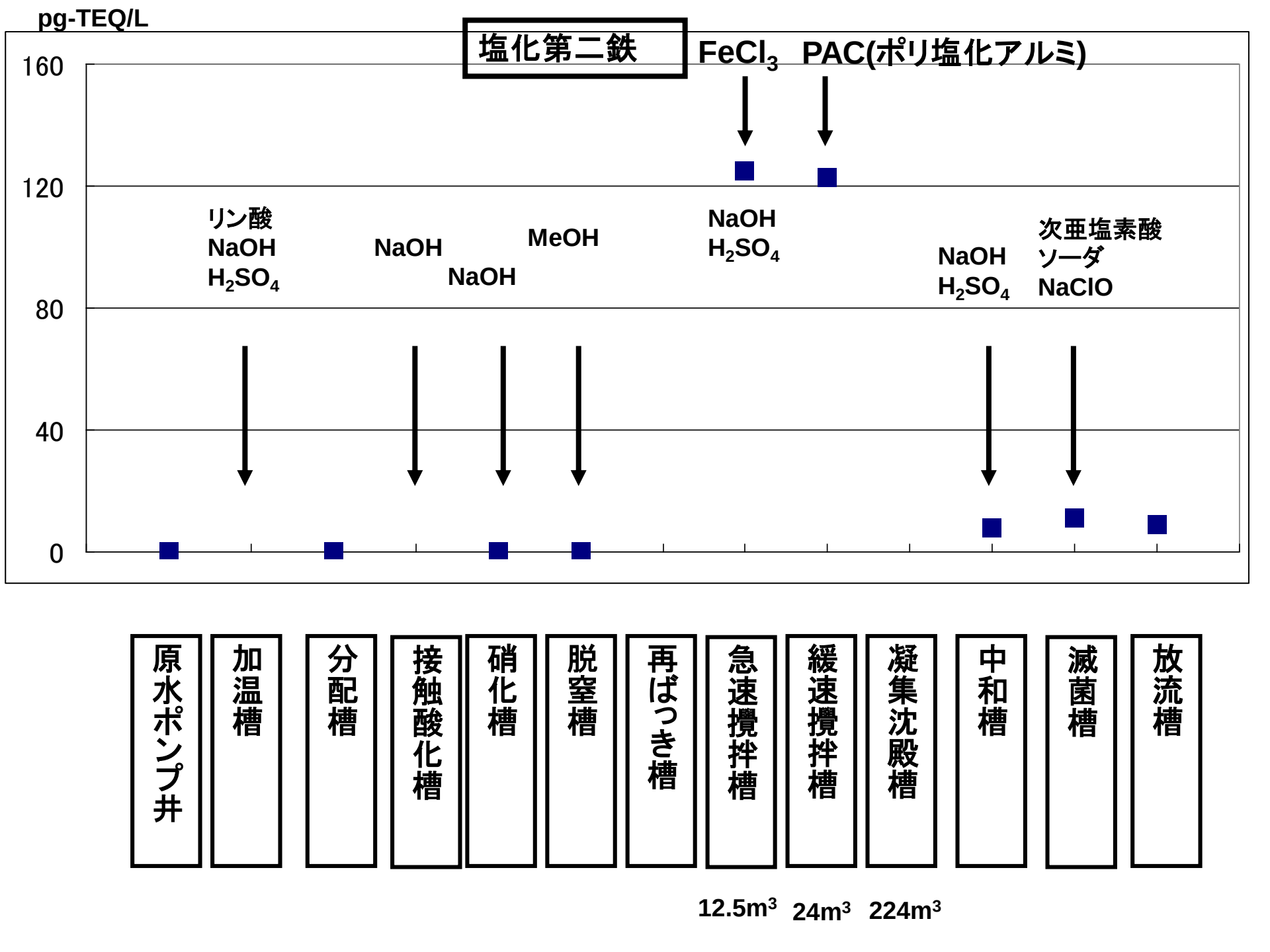
$FeCl_3$

3,3’-dichlorobenzidine

Chlorinated Paraffins

Diphenyl Silane diol

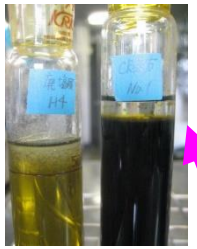
Organic pigment


pg-TEQ/L
塩化第二鉄
FeCl3
PAC(ポリ塩化アルミ)
160
120
80
40
0
リン酸
NaOH
H2SO4
NaOH
NaOH
MeOH
NaOH
H2SO4
NaOH
H2SO4
次亜塩素酸
ソーダ
NaClO
原水ポンプ井
加温槽
分配槽
接触酸化槽
硝化槽
脱窒槽
再ばっき槽
急速攪拌槽
緩速攪拌槽
凝集沈殿槽
中和槽
滅菌槽
放流槽
12.5m3
24m3
224m3

塩化第二鉄液製造フロー

鉄スクラップ
薄板端材、プレス屑

廃塩酸
鉄鋼 酸洗液
$HCl+FeCl_2$



廃塩化第二鉄液
エッチング使用済液
$FeCl_2+FeCl_3$

プリント基板

原料タンク

塩化第一鉄化
鉄溶解槽
$2HCl+Fe \rightarrow FeCl_2+H_2$

$2FeCl_3+Fe \rightarrow 3FeCl_2$

濃度調整

ろ過

銅回収

ろ液タンク

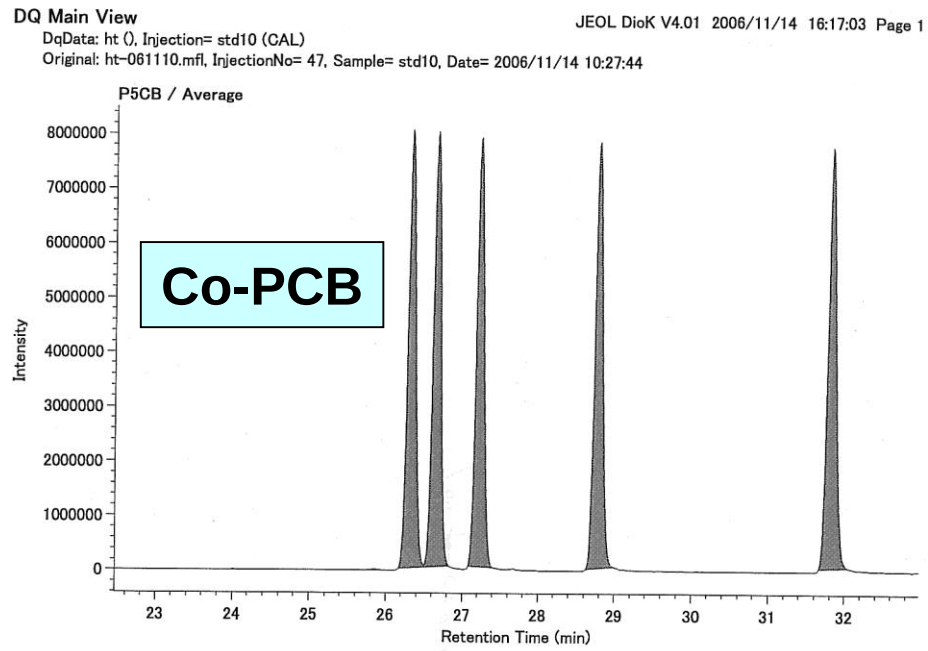
塩素ガス

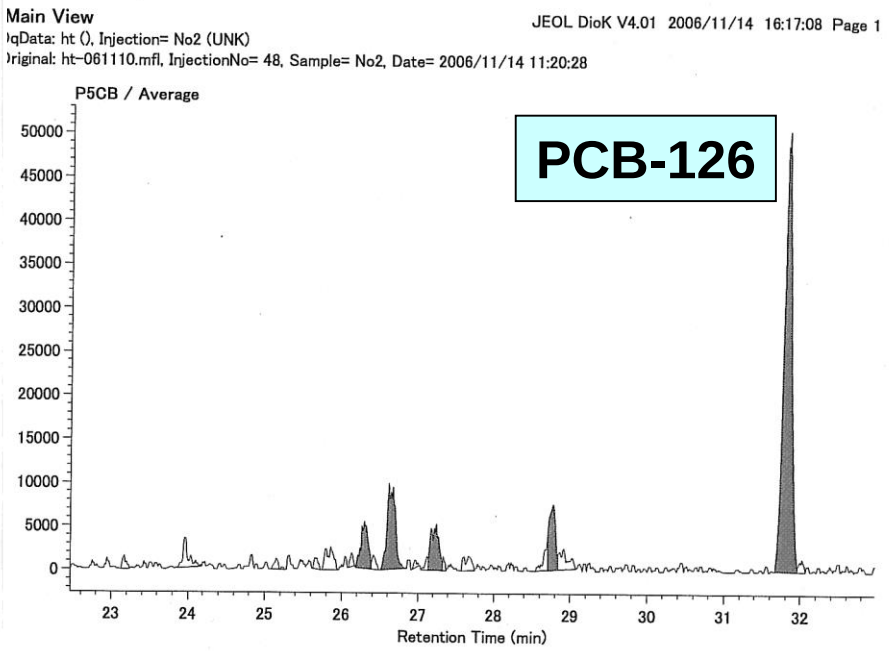
塩素化
$2FeCl_2+Cl_2 \rightarrow 2FeCl_3$

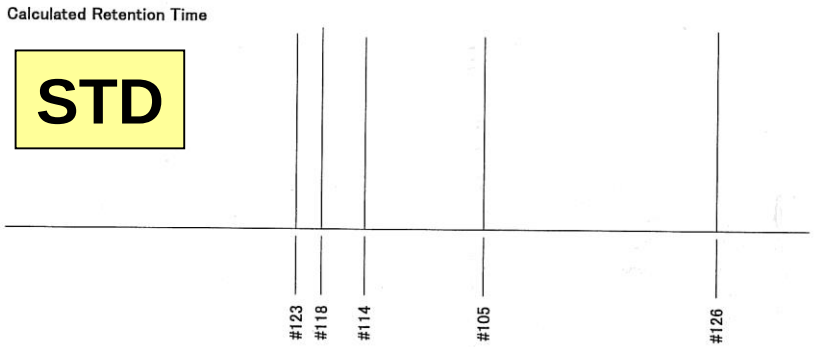
製品タンク

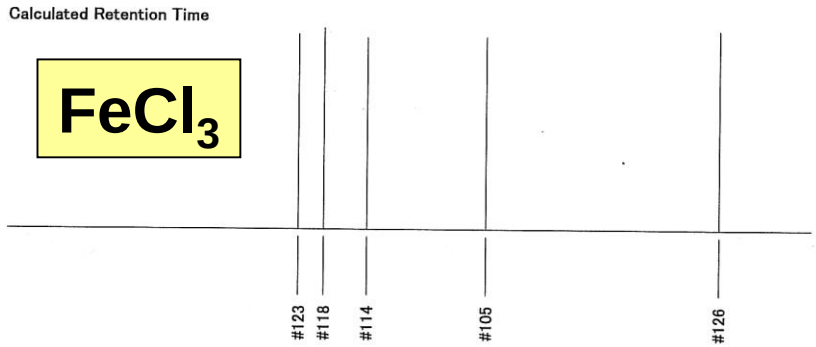
エッチング液
凝集沈殿剤

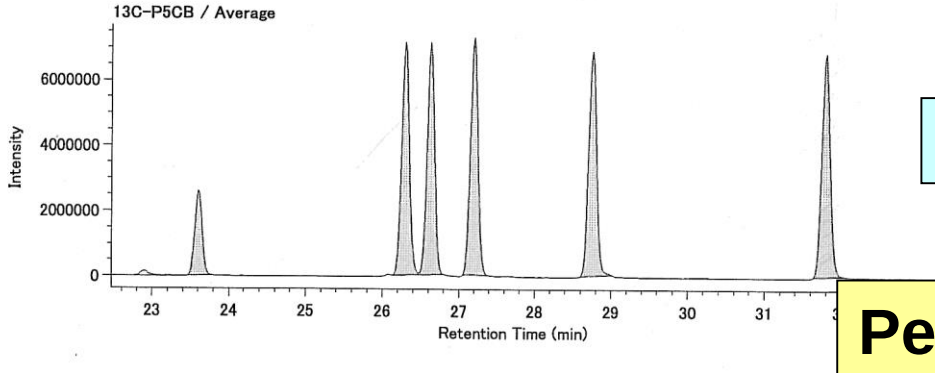
50-120m³

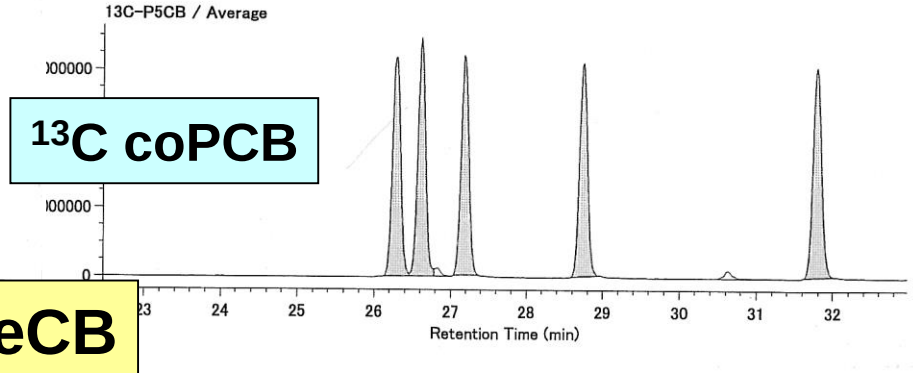

DQ Main View
JEOL DioK V4.01 2006/11/14 16:17:03 Page 1
DqData: ht (), Injection= std10 (CAL)
Original: ht-061110.mfl, InjectionNo= 47, Sample= std10, Date= 2006/11/14 10:27:44
P5CB / Average
Intensity
Retention Time (min)
Co-PCB


Main View
JEOL DioK V4.01 2006/11/14 16:17:08 Page 1
qData: ht (), Injection= No2 (UNK)
riginal: ht-061110.mfl, InjectionNo= 48, Sample= No2, Date= 2006/11/14 11:20:28
P5CB / Average
Retention Time (min)
PCB-126


Calculated Retention Time
STD
#123
#118
#114
#105
#126

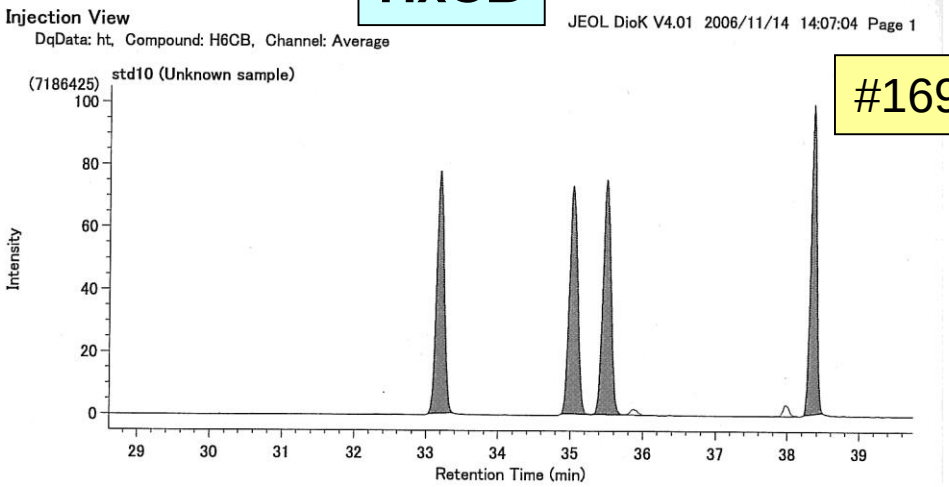

Calculated Retention Time
FeCl3
#123
#118
#114
#105
#126


13C-P5CB / Average
Intensity
Retention Time (min)
PeCB


13C-P5CB / Average
13C coPCB
Retention Time (min)

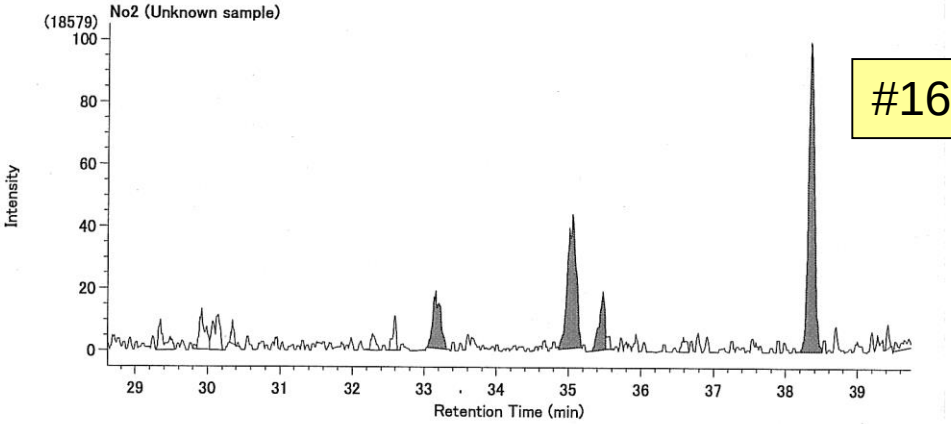
HxCB

STD



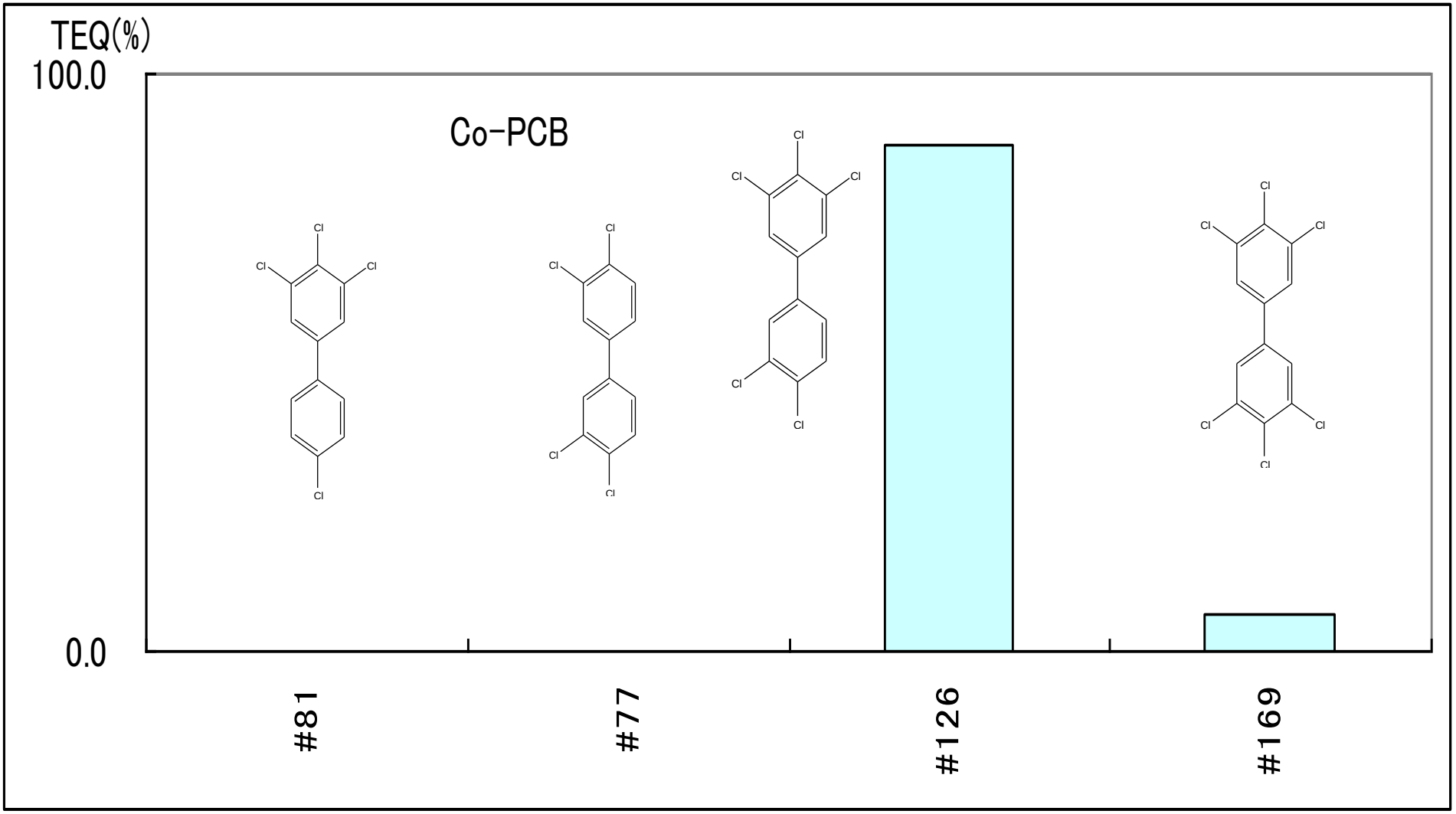
#169

$FeCl_3$



#169

塩化第二鉄$FeCl_3$液中には
Co-PCBのみが主要に検出
PeCBは　#126
HxCBは　#169



TEQ contributions (%) of co-PCB in $FeCl_3$

PCB CONGENER PROFILE OF UNINTENTIONAL FORMATION FROM PIGMENT MANUFACTURING PROCESS

$FeCl_3$

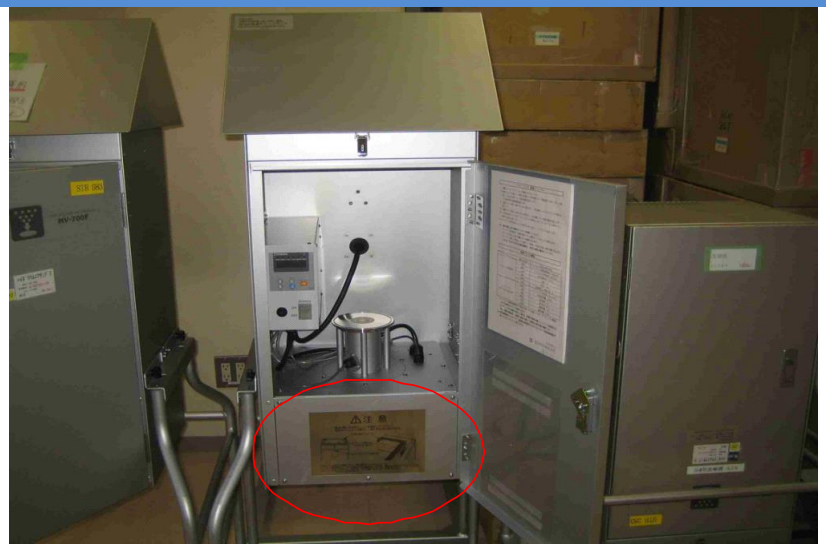
3,3’-dichlorobenzidine

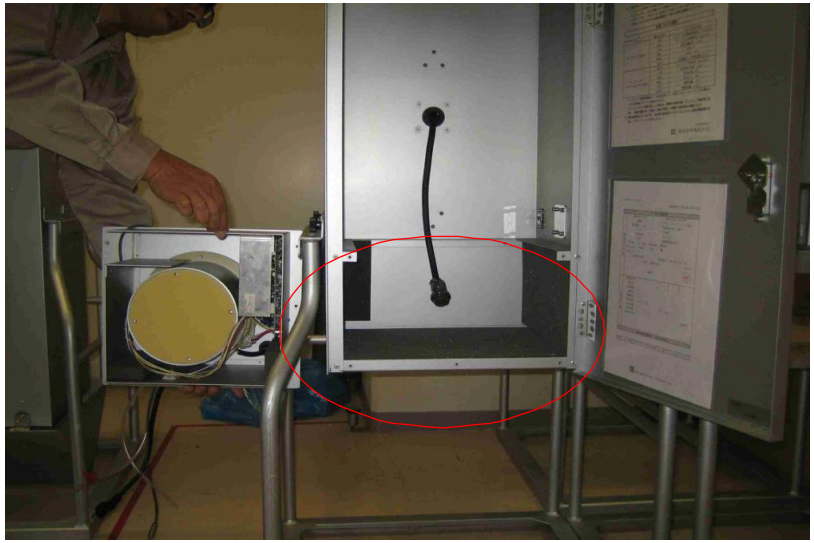
Chlorinated Paraffins

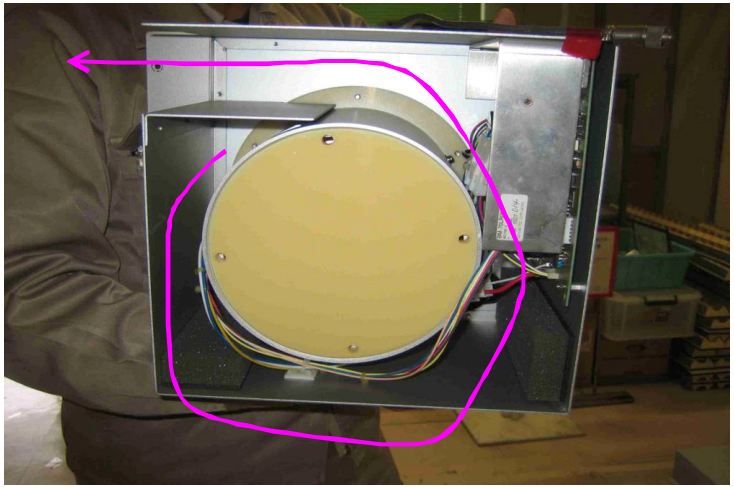
Diphenyl Silane diol

Organic pigment

High Volume Air Sampler







Noise/Vibration absorption rubber

Using chlorinated paraffins containing PCB

PCB CONGENER PROFILE OF UNINTENTIONAL FORMATION FROM PIGMENT MANUFACTURING PROCESS

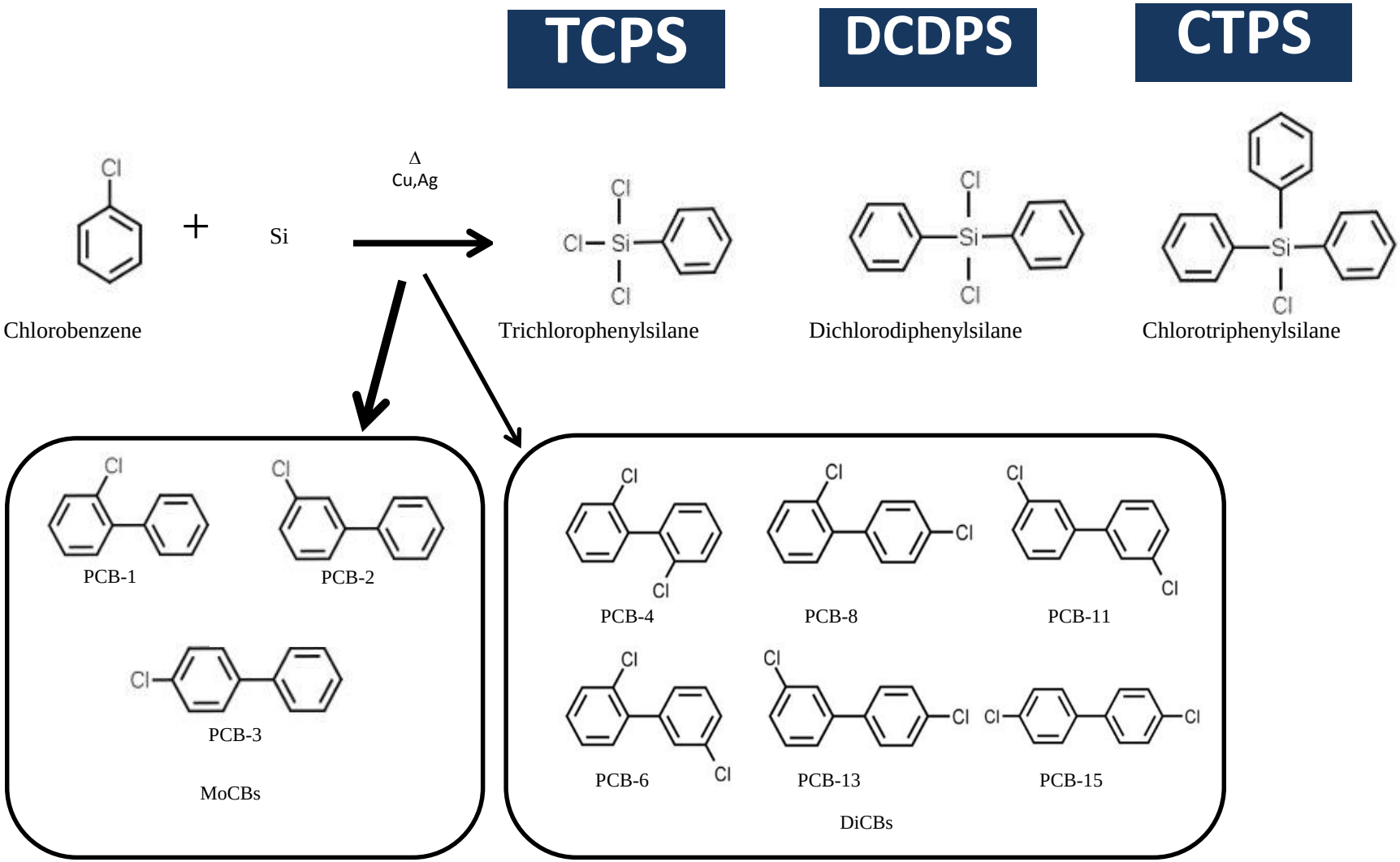
$FeCl_3$

Chlorinated Paraffins

3,3’-dichlorobenzidine

Diphenyl Silane diol

Organic pigment



dichlorodiphenylsilane

UNINTENTIONAL FORMATION OF PCB FROM CHEMICAL MANUFACTURING PROCESS

$FeCl_3$

3,3’-dichlorobenzidine

Chlorinated Paraffins

Diphenyl Silane diol

Organic pigment

Environ Sci Pollut Res (2014) 21:998–1009
DOI 10.1007/s11356-013-1977-2

RESEARCH ARTICLE

Concentration levels and congener profiles of polychlorinated biphenyls, pentachlorobenzene, and hexachlorobenzene in commercial pigments

Katsunori Anezaki · Takeshi Nakano

Received: 10 April 2013 / Accepted: 2 July 2013 / Published online: 14 July 2013

Abstract The concentration levels and congener profiles of polychlorinated biphenyls (PCBs), pentachlorobenzene (PeCBz), and hexachlorobenzene (HxCBz) were assessed in commercially available organic pigments. Among the azo-type pigments tested, PCB-11, which is synthesized from 3,3′-dichlorobendizine, and PCB-52, which is synthesized from 2,2′,5,5′-tetrachlorobendizine, were the major congeners detected. It is speculated that these were byproducts of chlorobendizine, which has a very similar structure. The total

study detected a certain level of PCB-11, which is not included in PCB technical mixtures, and revealed continuing PCB pollution originating from pigments in the ambient air.

Keywords Polychlorinated biphenyls · Congeners · Hexachlorobenzene · Pentachlorobenzene · Pigments · Ambient air · Byproduct

Environ Sci Pollut Res
DOI 10.1007/s11356-014-2985-6

Polychlorinated biphenyl contamination of paints containing polycyclic- and Naphthol AS-type pigments

Katsunori Anezaki · Narayanan Kannan · Takeshi Nakano

Received: 2 March 2014 / Accepted: 28 April 2014

Abstract This study reports the concentrations and congener partners of polychlorinated biphenyls (PCBs) in commercially available paints. Polycyclic-type pigments containing dioxazine violet (pigment violet (PV) 23, PV37) and diketopyrrolopyrrole (PR254, PR255) were found to contain PCB-56, PCB-77, PCB-40, PCB-5, and PCB-12, and PCB-6, PCB-13, and PCB-15, respectively, as major congeners. Dioxazine violet is contaminated with by-products during synthesis from *o*-dichlorobenzene, which is used as a solvent during synthesis, and diketopyrrolopyrrole is contaminated with by-products during 3.8 mg/kg, respectively. The corresponding TEQ for PR112 was 0.0039–8.6 pg-TEQ/g.

Keywords Polychlorinated biphenyls · Congeners · Pigments · Dioxazine violet · Diketopyrrolopyrrole · Naphthol AS · By-product

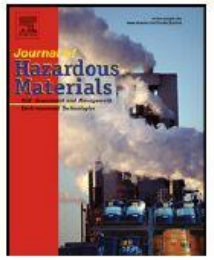
Introduction

Journal of Hazardous Materials 287 (2015) 111–117

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat



Unintentional PCB in chlorophenylsilanes as a source of contamination in environmental samples

Katsunori Anezaki [a,*], Takeshi Nakano [b]

[a] Hokkaido Research Organization, Environmental and Geological Research Department, Institute of Environmental Sciences, N19W12, Kita, Sapporo, Hokkaido, Japan

[b] Center for Advanced Science and Innovation, Osaka University, Osaka, Japan

- PCB in silicone-based adhesives and chlorophenylsilanes
- Congener profiles in adhesives and chlorophenylsilanes : ------- > quite similar
- High PCBs were detected in dichlorodiphenylsilane.

- Similar Congener profiles were come from the chlorobenzene used for chlorophenylsilanes manufacturing process.

はじめに

化成品工業協会 自主測定

一部の有機顔料 → 製造工程で非意図的生成PCB含有

経済産業省　事業者に指導

国際的な基準を超える有機顔料 → 製造、輸入及び出荷を停止

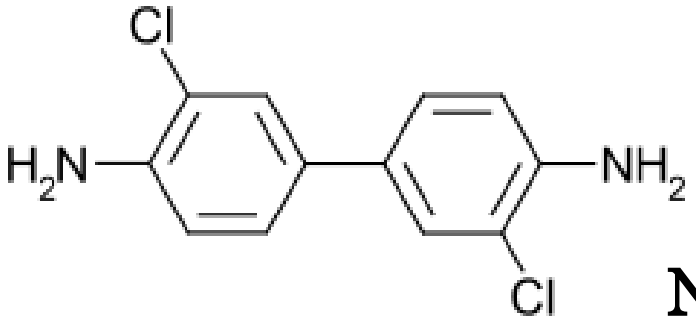
はじめに

顔料 → 着色に用いる粉末
水や油に不溶なものの総称

有機顔料 → 有機化合物を成分とする顔料

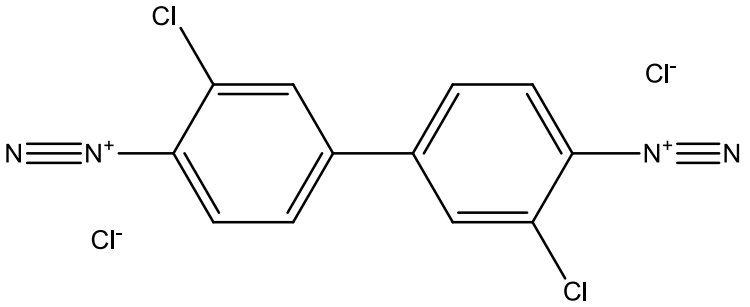
アゾ顔料（モノアゾ, ジスアゾ, ピラゾロン）PY, PO, PR
フタロシアニン顔料（PG）多環式顔料（PV, PR）

PCB測定・異性体組成の特徴

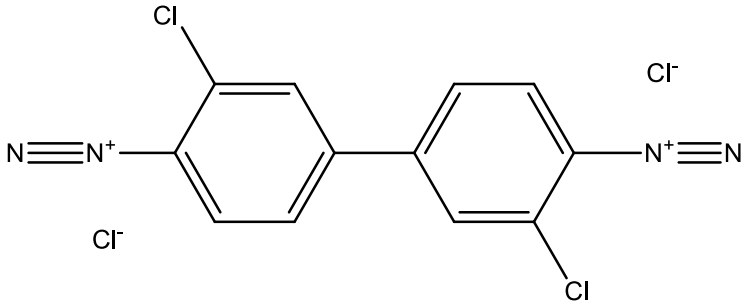


3,3’-ジクロロベンジジン

$NaNO_2$, HCl

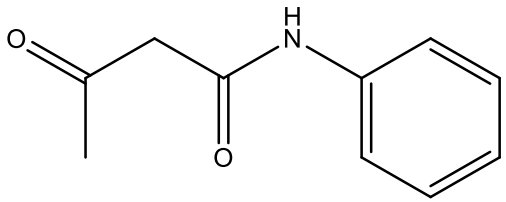


ジアゾニウム塩

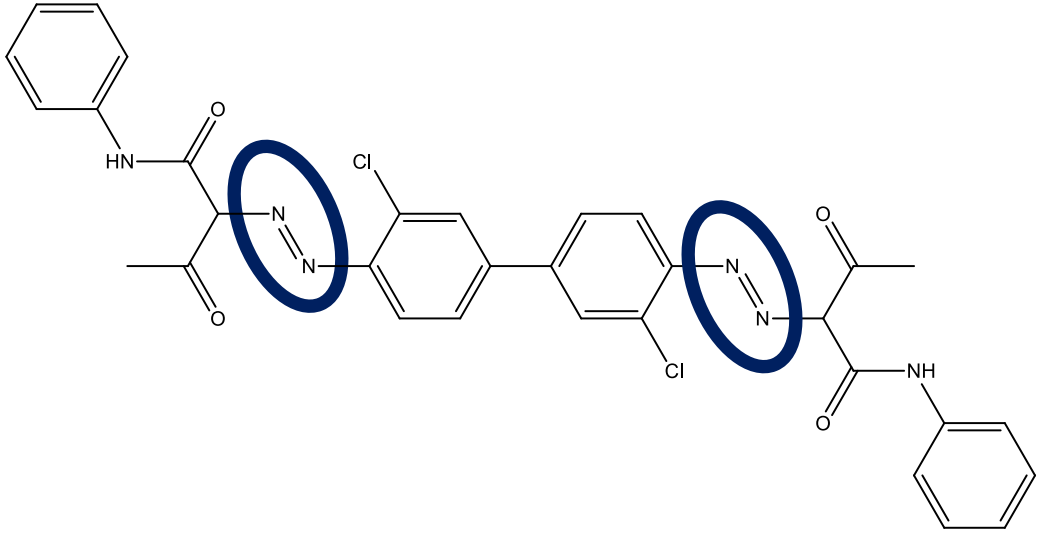


ジアゾニウム塩

＋

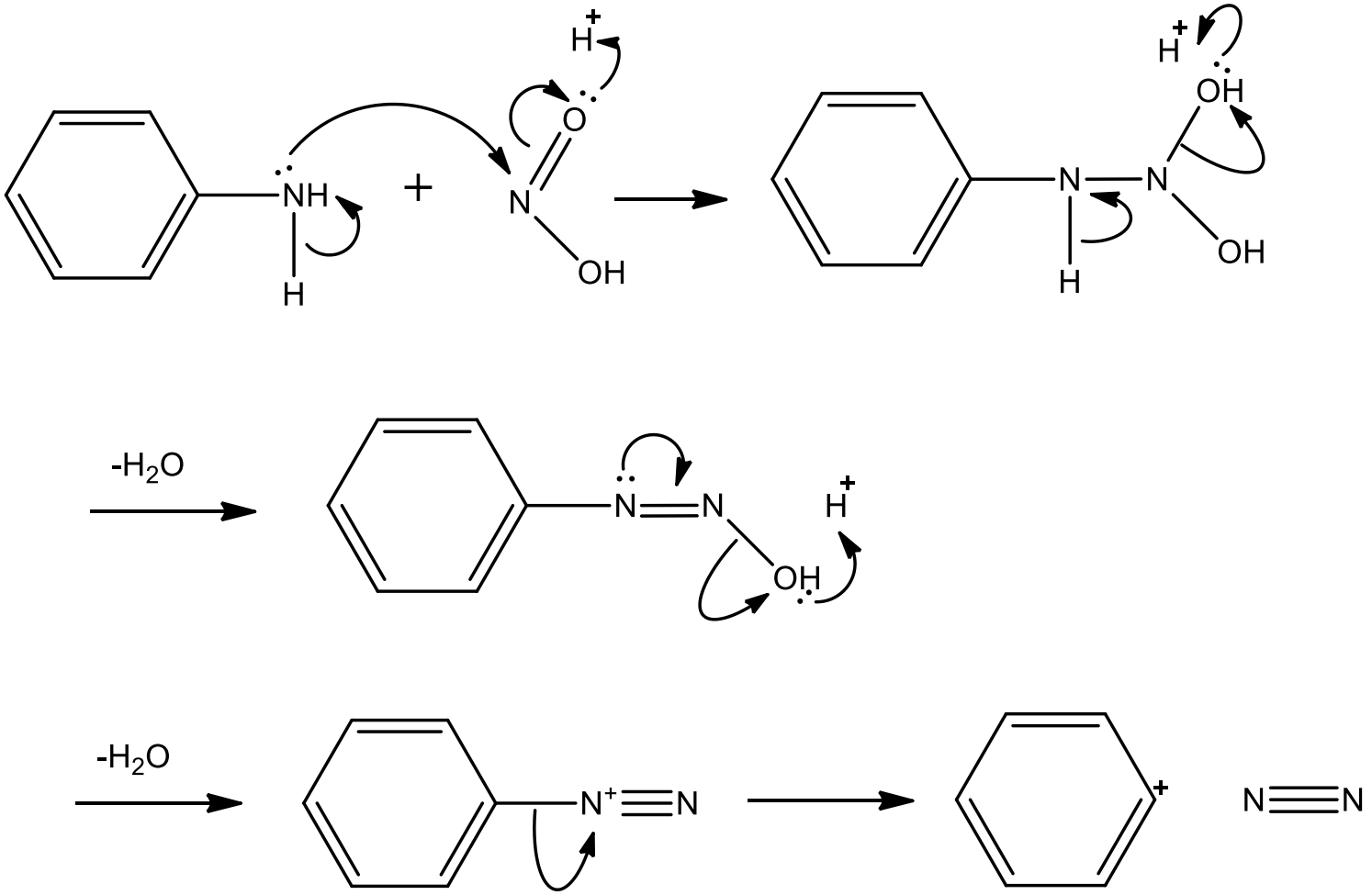


N－アセトアセチルアニリン



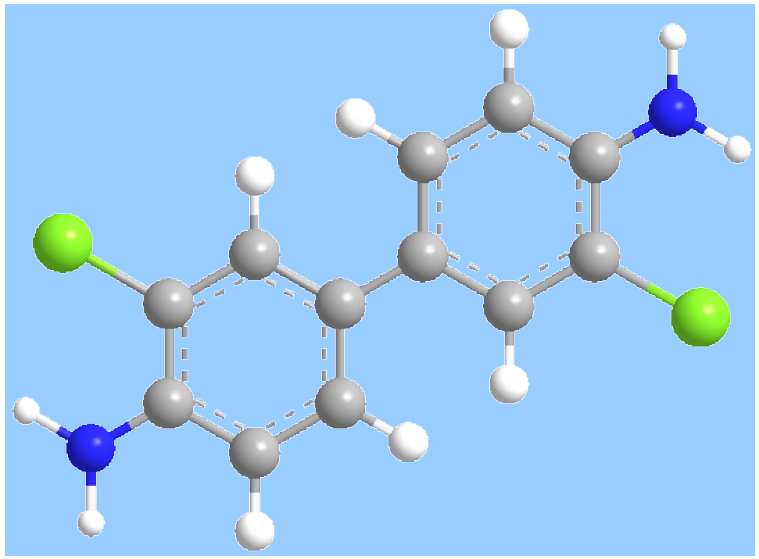
ジスアゾ系

顔料の合成過程の例

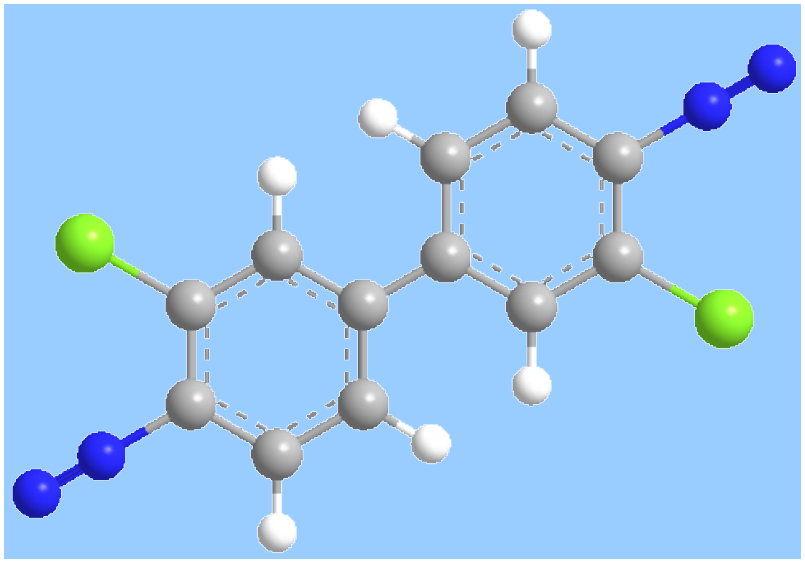


ジアゾニウム塩の生成と分解

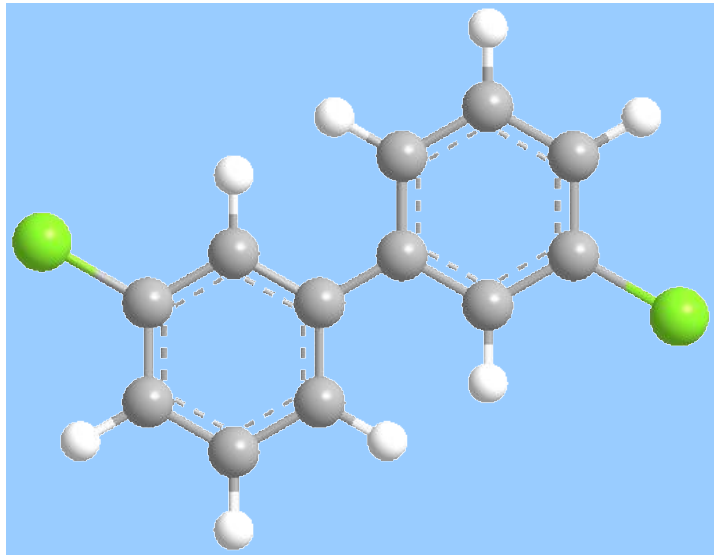
アミンを酸性水溶液中で亜硝酸塩に作用させると、速やかにジアゾニウム塩を生成する。



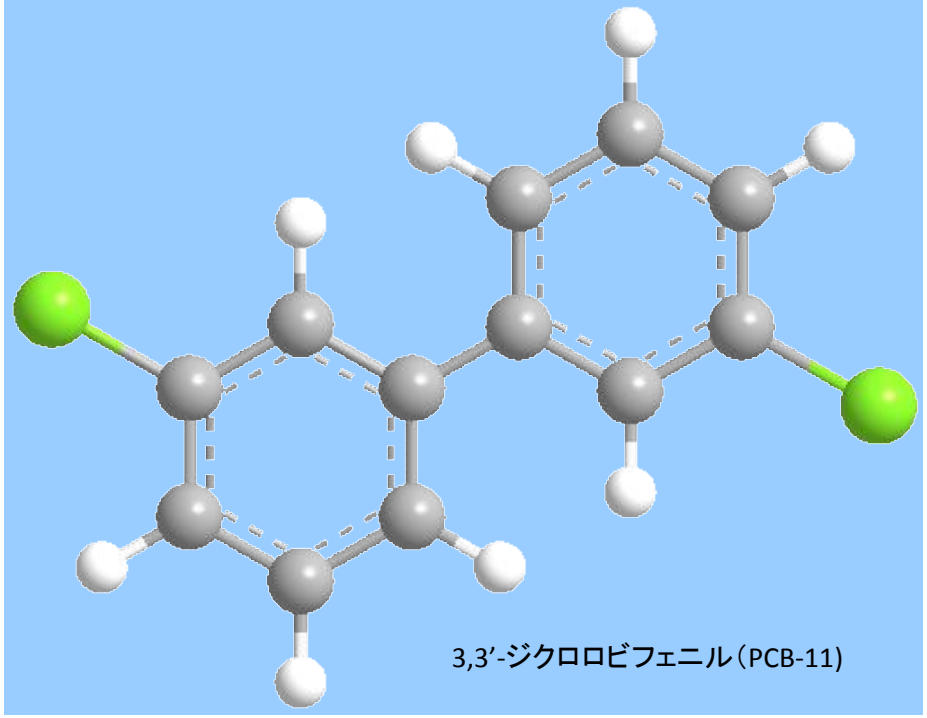
3,3’-ジクロロベンジジン



（ジアゾニウム塩）



3,3’-ジクロロビフェニル（PCB-11)



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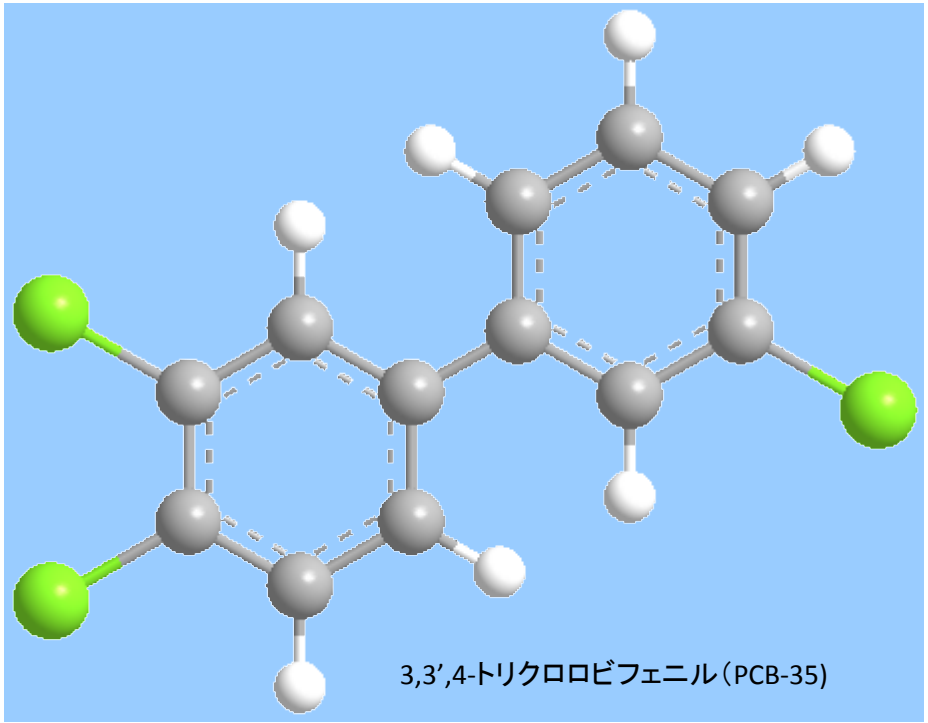
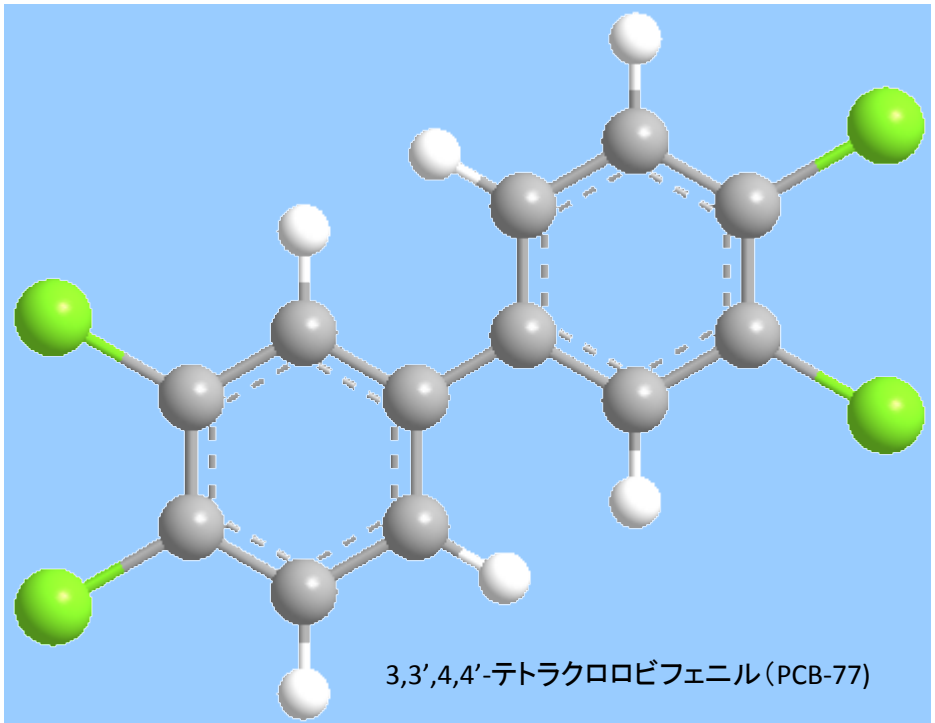
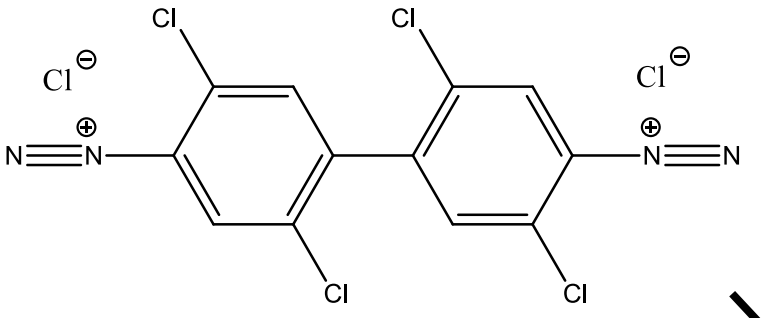
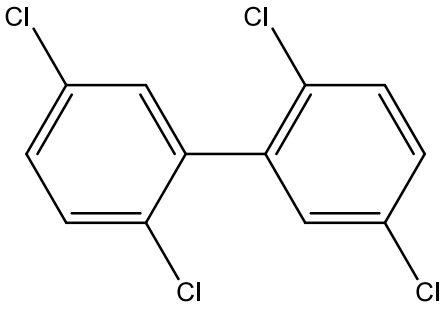


3,3’,4-トリクロロビフェニル（PCB-35)



3,3’,4,4’-テトラクロロビフェニル（PCB-77)

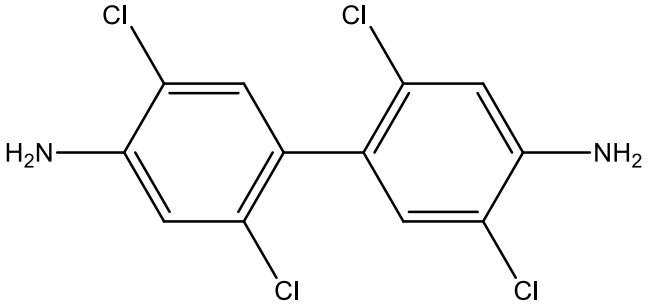


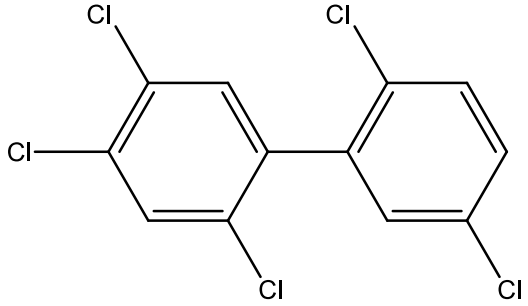


CB-52(25-25)

$NaNO_2$, HCl

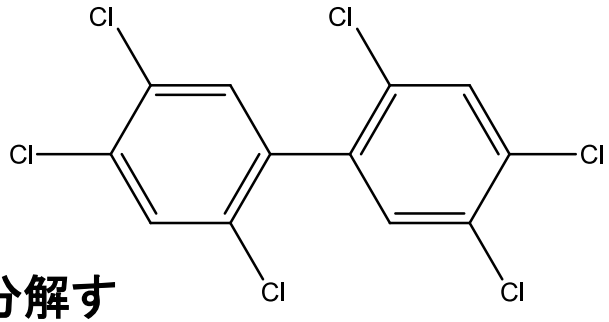
$(CuCl_2)$





CB-101(245-25)

2,2',5,5'-テトラクロロベンジジン

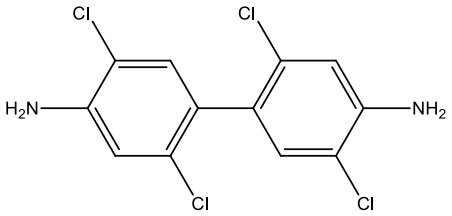


CB-153(245-245)

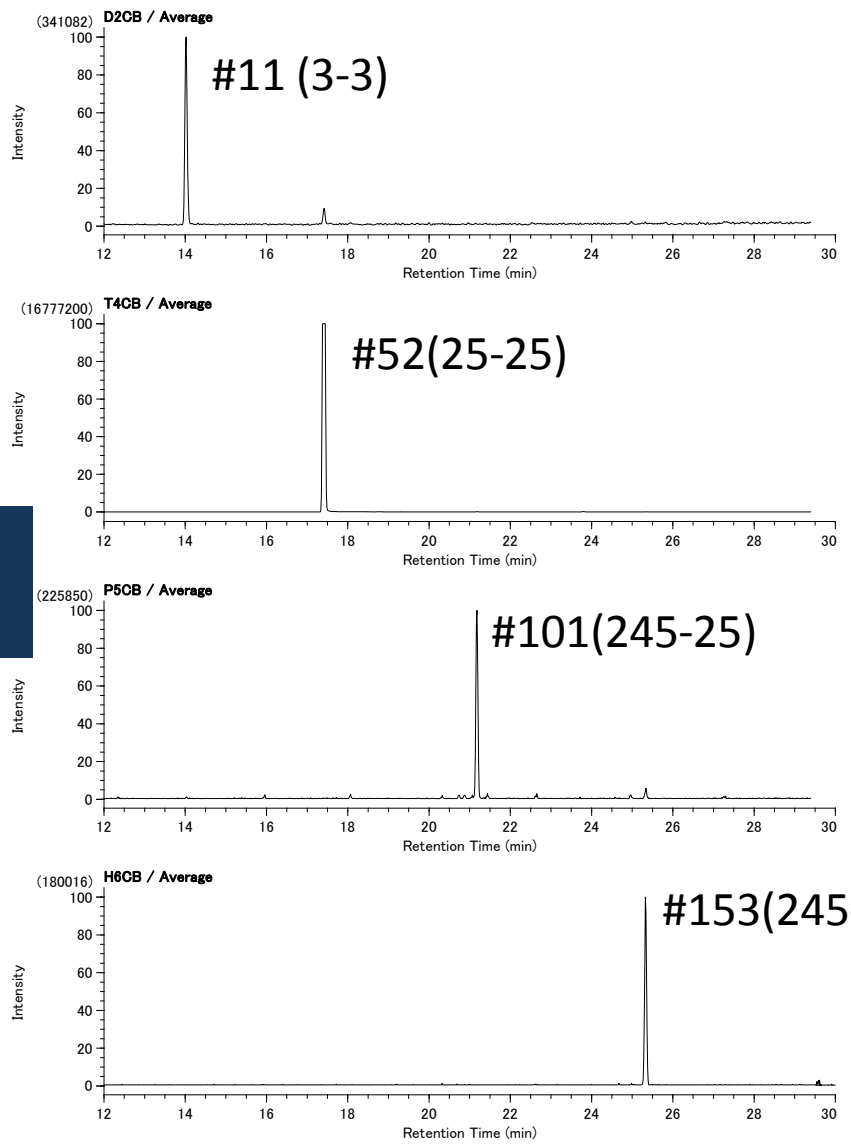
サンドマイヤー反応

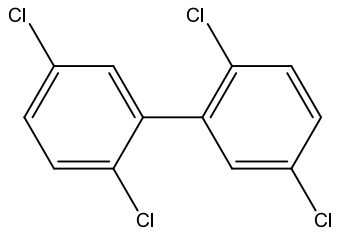
$Ar\text{-}N^{+}\equiv N + CuX \rightarrow Ar\text{-}X + Cu^{+} + N_2\uparrow$

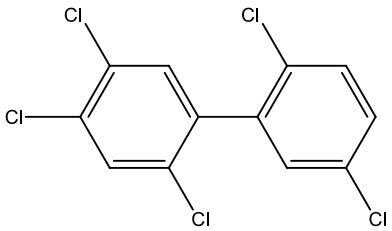
芳香族ジアゾニウム塩を塩化銅(存在下に生成させ、加温分解すると、アミノ基が塩素置換されたアリールが生成

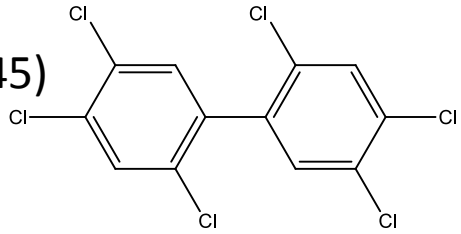


2,2',5,5' –
テトラクロロベンジジン



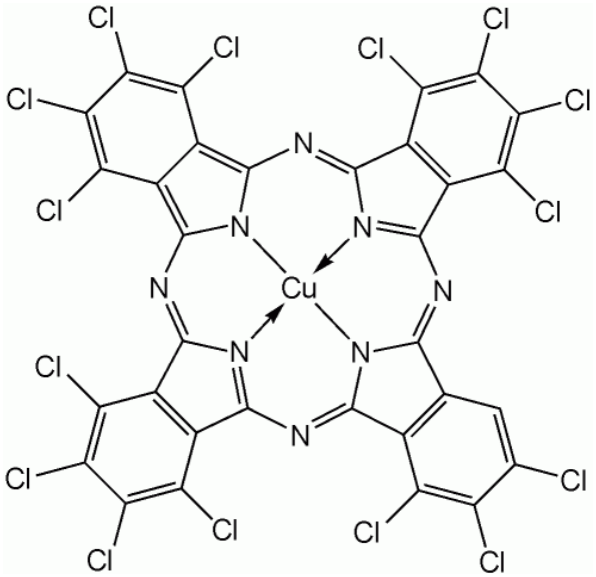






顔料中のPCB異性体（ジスアゾ系）
permanent yellow lemon; PY81;

phthalocyanine-type pigment



pigment green 7
(phthalocyanine green)

raw material

phthalic anhydride
urea
copper chloride

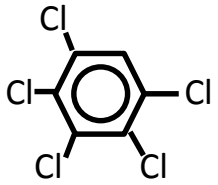
↓

pigment blue 15
(phthalocyanine blue)

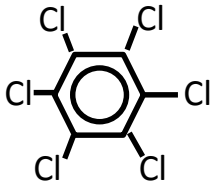
↓ chlorination
↓ Δ

pigment green 7

By-product

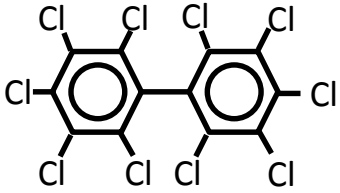


PeCBz

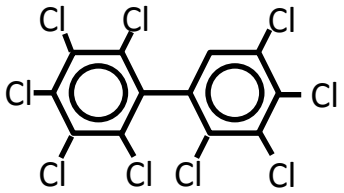


HCB

PG-7



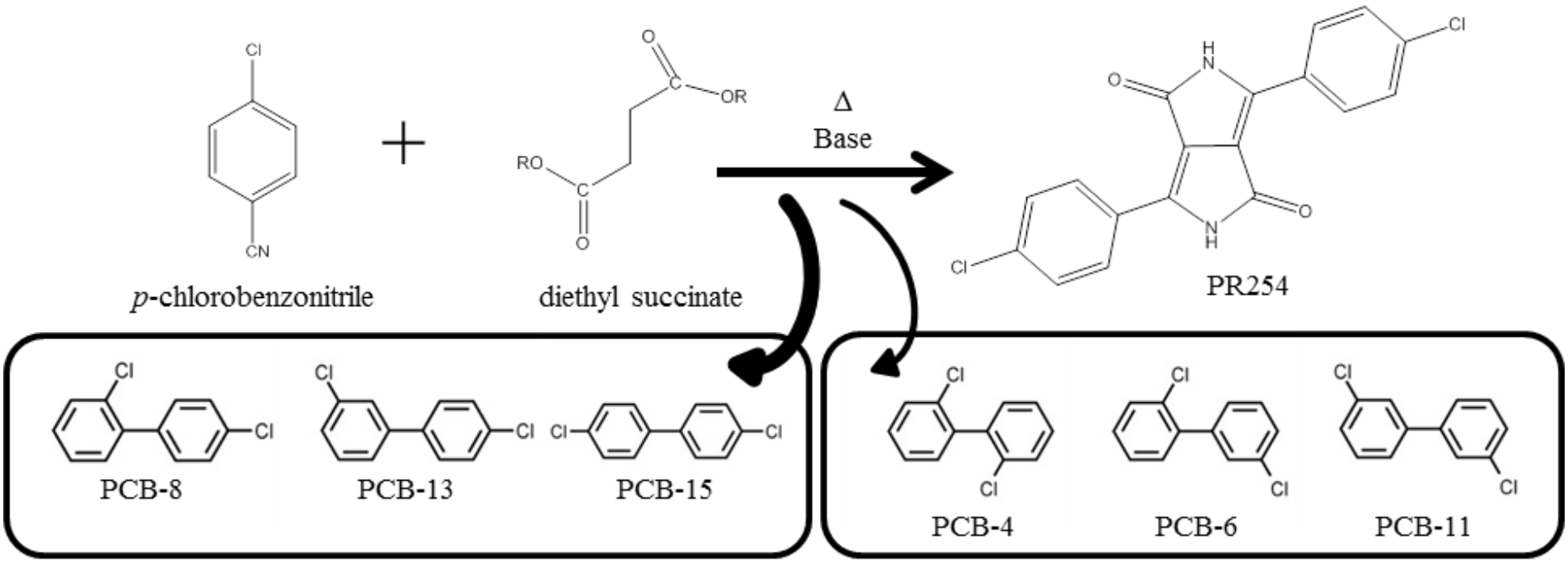
#209



#208

highly chlorinated PCBs

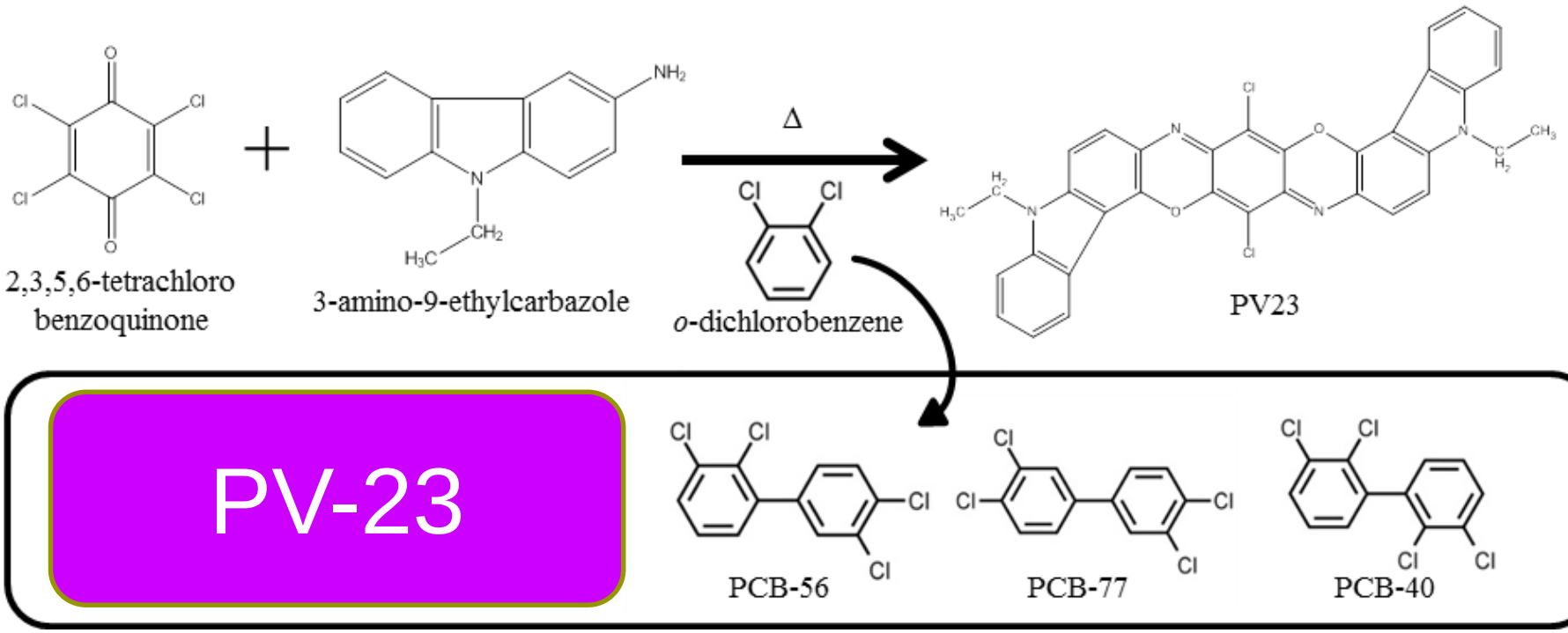
PCB congener profiles of diketo-pyrrolo-pyrrole pigments



PR-254

PCB-8, PCB-13, PCB-15 >> PCB-4, PCB-6, PCB-11

PCB congener profiles of dioxazine violet pigments



- 結果

-有機顔料中の副生PCB異性体

- 3,3’ージクロロベンジジンを原料とする顔料
  #11, #35, #77を、
- 2,2’,5,5’-テトラクロロベンジジンを原料とする顔料
  #52, #101, #153を、
- フタロシアニン系顔料 （塩素化過程）
  #209, #208, #207, #206, PeCBz, HCB
- PV-23 (*o*-ジクロロベンゼン　還流溶媒）
  #5, #12, #56, #77, #40
- PR-254 (*p*-クロロベンゾニトリル　原料）
  #8, #13, #15, #4, #6, #11

顔料由来の異性体と
環境試料中のPCB

Identification of a novel PCB source through analysis
of 209 PCB congeners by US EPA modified method 1668

Simon Litten et al, *Chemosphere*, 46, 1457-1459(2002)

PISCES survey, 7/27/00–8/2/00 to locate sources of PCB congeners (ng/l)

	Total PCB	PCB-11	PCB-35	PCB-77	PCB-126	TEQ(fg/L)
Pigment discharge	4200	3600	380	190	1.6	18000
WPCF influent	520	490	2.3	2.5	0.01	150
Trunk1	18	0.07	0	0	<0.001	15
Trunk2	12	0.4	0.02	0.01	<0.0004	13
Trunk3	12	0.6	0.03	0.01	<0.001	8
Trunk4	3	0.08	0.04	0.05	<0.001	2
Trunk5	1	0.2	0.02	0.04	0.001	1

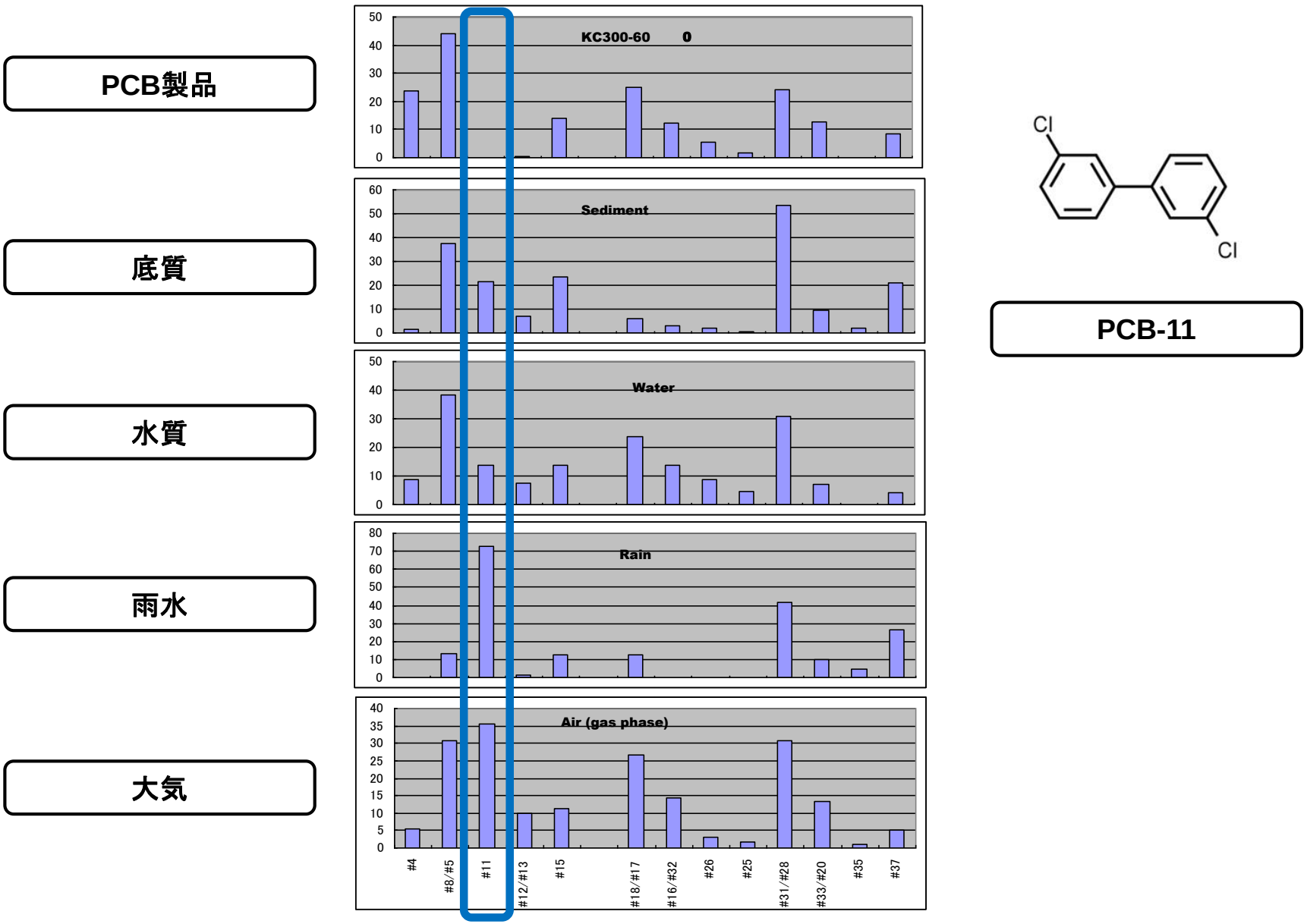


図　PCB製品および環境試料中のDi-TrCB異性体分布 #10/(2,6-)#4(2,2'-), #8(2,4-)/#5(2,3-), #11(3,3'-), #12(3,4-)/#13(3,4'), #15(4,4'-), #18(2,2',5-)/#17(2,2',4-), #16(2,2',3-)/#32(2,4',6-), #26(2,3',5-), #25(2,3',4-),#31(2,4',5-)/#28(2,4,4'-),#33(2',3,4-)/#20(2,3,3'-),#35(3,3',4-), #37(3,4,4'-)

中野ら, 環境化学討論会要旨集 74,1433-1436 (2001)

底質

底質

河川水

河川水

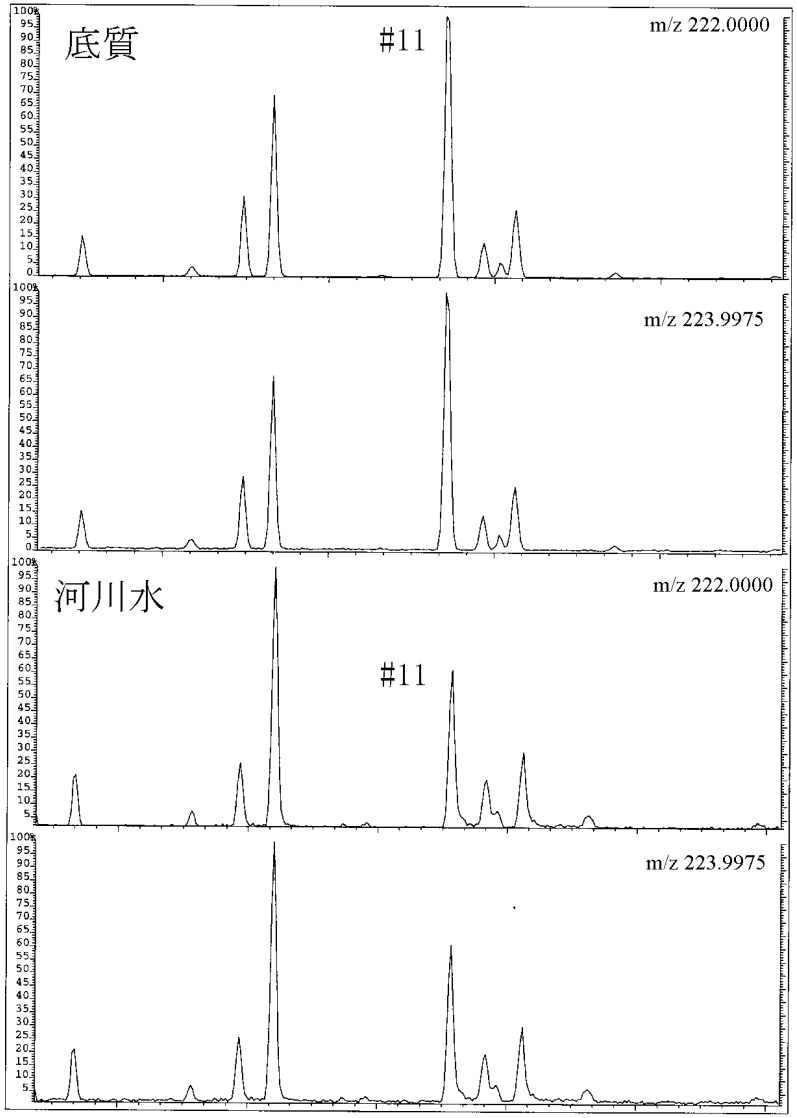


図　底質、表層水中の2塩素化ﾋﾞﾌｪﾆｰﾙのSIMｸﾛﾏﾄｸﾞﾗﾑ
#10/(2,6-)#4(2,2'-), #8(2,4-)/#5(2,3-), #11(3,3'-), #12(3,4-)/#13(3,4'), #15(4,4'-)

角谷ら, 環境化学討論会要旨集 74,1433-1436 (2001)

顔料由来の異性体と
環境大気中のPCB

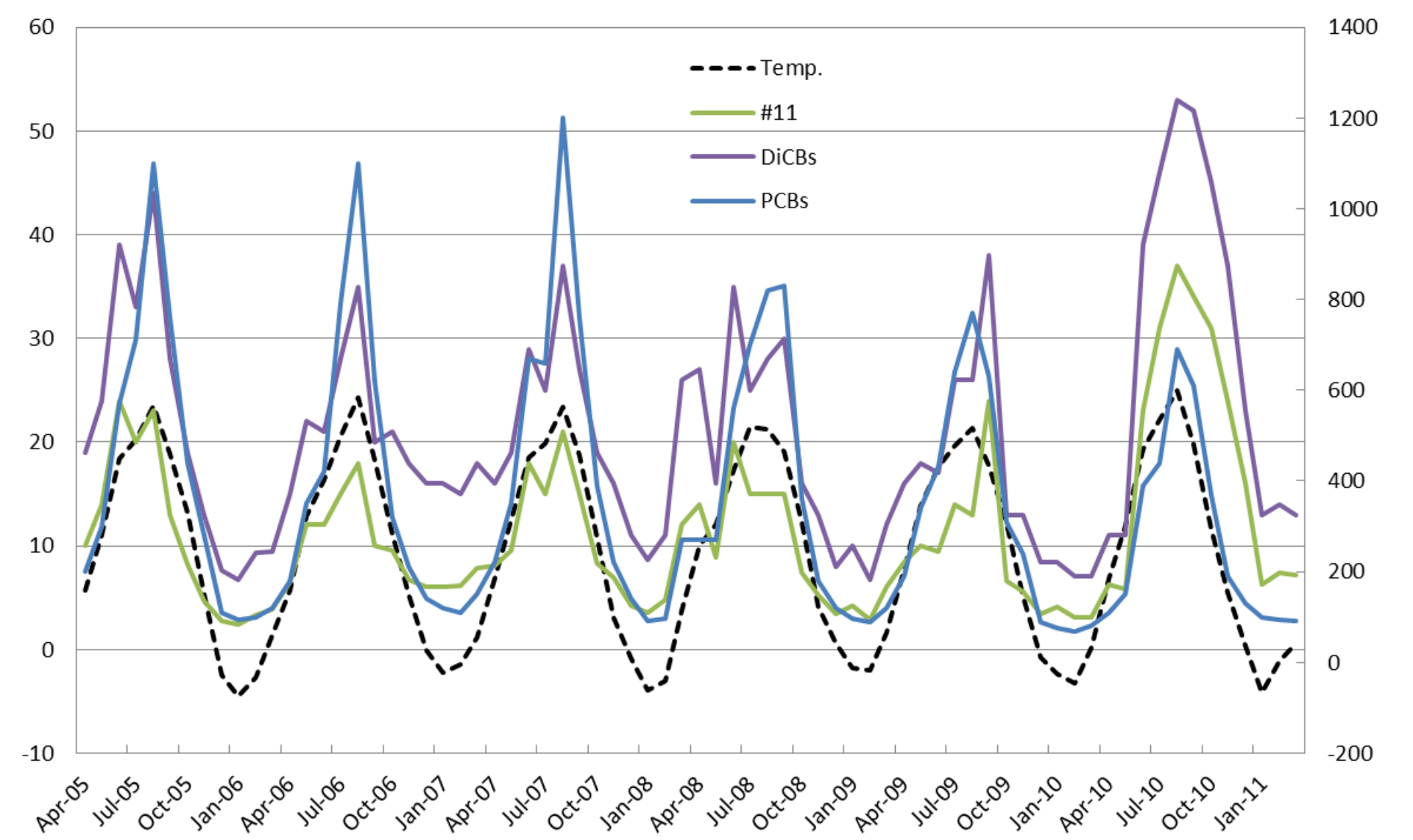
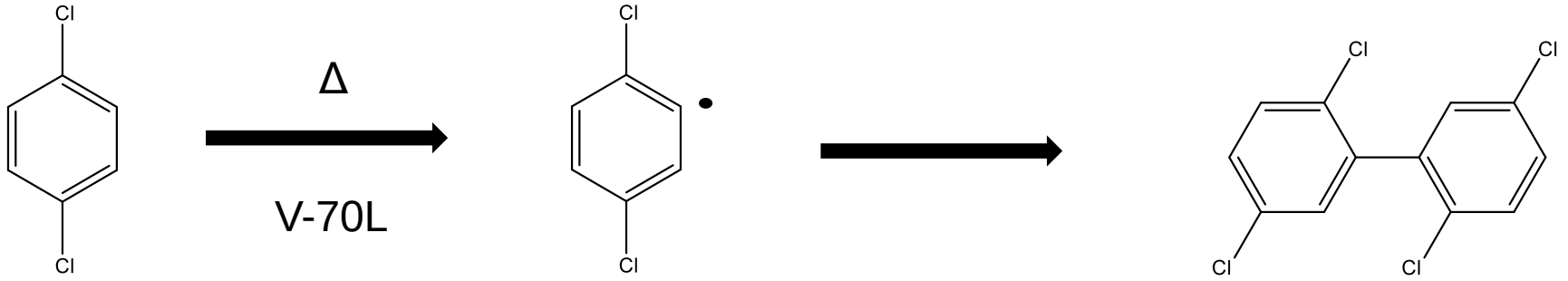


Fig. 3 Seasonal variations of PCBs, DiCBs and #11 congener in Sapporo

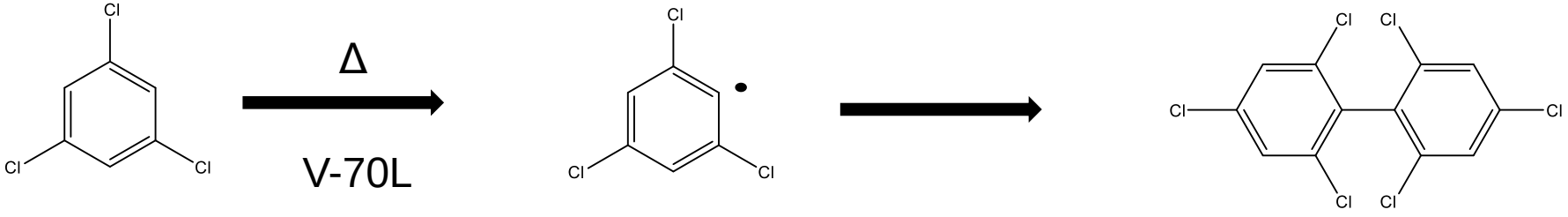
Anezaki et al, *organohalogen compounds* 74,1433-1436 (2012)

one PCB isomer formation



CB-52 (25-25)

p-dichlorobenzene

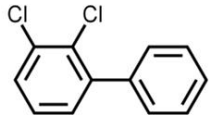


CB155 (246-246)

1,3,5-trichlorobenzene

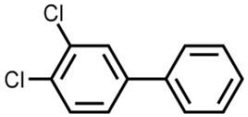
CB-56 > CB-77 > CB-40

A B > BB > AA



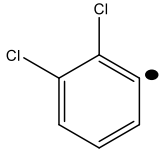
5

CB-5 (23-)



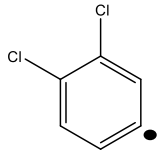
3

CB-12 (34-)



A

AB

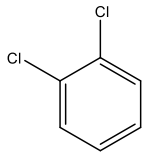


B

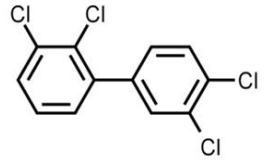
BB

V-70L

Δ

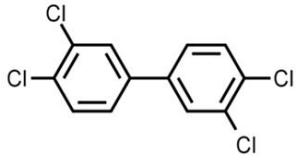


AA



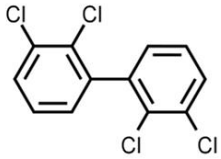
11

CB-56 (23-34)



5

CB-77 (34-34)



2

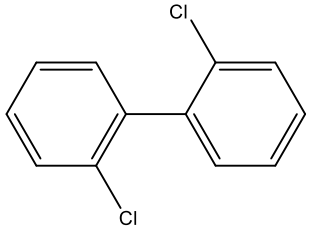
CB-40 (23-23)

o-dichlorobenzene

CB-6 > CB-8 > CB-11, CB-13 > CB-4 > CB-15

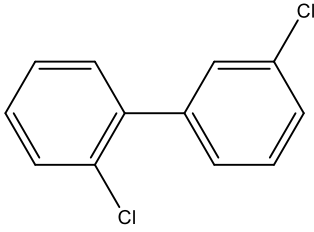
A B > AC > BB , BC > AA > CC

AA



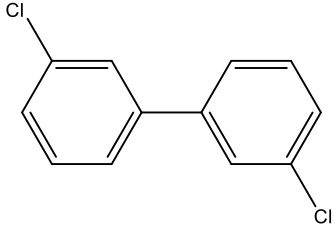
CB-4 (2-2)

AB

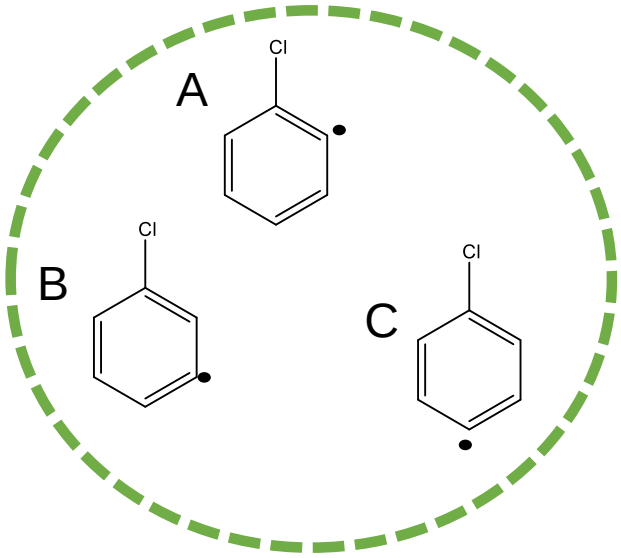


CB-6 (2-3)

BB

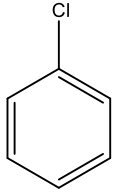


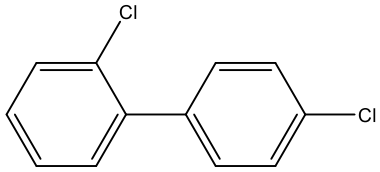
CB-11 (3-3)



V-70L

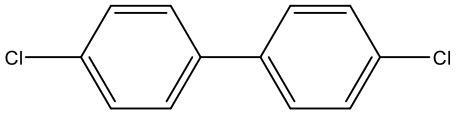
Δ





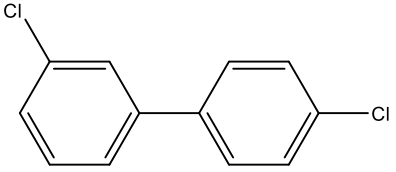
AC

CB-8 (2-4)



CC

CB-15 (4-4)



BC

CB-13 (3-4)

chlorobenzene → DiCB

Computational Method: *Ab initio* Calculations

Geometry Optimization:

Ab initio Density Functional Theory (DFT): B3LYP/6-311g(d)

Ab initio Molecular Orbital method: HF/6-311g(d)

Molecular Orbitals:

Ab initio Molecular Orbital method: HF/6-311g(d)

Solvated Systems:

Self-Consistent Reaction Field: SCRF

Isodensity surface polarized continuum mode (IPCM)

Dichlorobenzene ε=9.93

日本語

The 9th International PCB Workshop

Welcome to The 9th International PCB Workshop!

Date: Oct. 9-13th, 2016

Venue: Kobe Convention Center

Access: Port Island, Kobe, Japan

What is the PCB Workshop?

Scientists working on halogenated compounds gather biennially for the interdisciplinary discussions focusing especially on PCBs.

Official language is English.