catalysts

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Supplementary Materials:

Hydrodechlorination of different chloroaromatic compounds at room temperature and ambient pressure — differences in reactivity of Cu- and Ni-based Al alloys in an alkaline aqueous solution

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No. of Figures: 6

Table S1: Composition of the reaction mixtures obtained by overnight action of 1.5 g the Dev. alloy and 2 g NaOH in 200 mL of aqueous (or 1:1 CH_3OH : H_2O) solution containing 10 µmol of appropriate Ar-Cl.

HDC treated	Ar-Cls distribution after HDC reaction (mol. %)										
Ar-Cl	HCB	penta CB	Tetra CB	1,2,3-triCB	1,2,4-triCB	1,3,5-triCB	1,2-DCB	1,3-DCB	1,4-DCB	CB	B
HCB	0	0	22.90	0	0	0	29.40	18.70	18.70	10.30	0
HCB*	78.20	0	20.40	0.30	1.10	0.02	0	0	0	0	0
Penta CB	-	1.27	69.40	0	8.64	0	4.90	3.35	2.67	6.27	3.50
Tetra CBs	-	-	45.40	2.00	22.10	8.10	3.30	2.50	2.40	10.30	3.90
triCB	-	-	-	29.86	40.06	22.48	1.57	2.71	0.72	0.25	2.36
DCB	-	-	-	-	-	-	30.33	35.31	28.24	4.14	1.98
DCB	-	-	-	-	-	-	90.6	0.27	0.35	3.40	5.40

* 0.3 g of the Devardas alloy and 1.2 g NaOH was used

Table S2: Composition of the reaction mixtures obtained by overnight action of 5 mmol $NaBH_4$ and eventually 2 mmol of $CuSO_4$ or $NiSO_4$ on 10 μmol of corresponding Ar-Cl in 200 mL solution of CH_3OH : H_2O = 1:1.

Observed products after HDC	HDC of hexachlorbenzene			HDC of mixture of tetrachlorbenzenes			HDC of 1,2,4-trichlorbenzene			
	$CuSO_4/NaBH_4$	$NiSO_4/NaBH_4$	$NaBH_4$	$CuSO_4/NaBH_4$	$NiSO_4/NaBH_4$	$NaBH_4$	$CuSO_4/NaBH_4$	$NiSO_4/NaBH_4$	$NaBH_4$	Al
HCB	0.06	0	0	-	-	-	-	-	-	-
pentaCB	0.46	0.055	41	-	-	-	-	-	-	-
tetraCB	34.81	0	38.32	94.72	0	98.3	-	-	-	-
1,2,3-triCB	0	0	0.974	0.48	0	0.19	-	-	-	-
1,2,4-triCB	11.84	0.065	6.03	4.58	0.21	0.33	89.15	9.33	93.25	100
1,3,5-triCB	0	0	7.06	0.22	0	0	-	-	-	-
1,2-DB	51.47	0	2.63	0	0	0.4	3.56	13.55	1.69	0
1,3-DB	0.63	0	0.526	0	0	0.22	2.59	3.83	1.07	0
1,4-DB	0.68	0	3.46	0	0	0.527	0	2.72	1.74	0
CB	0.04	0	0	4	0	0	1.6	1.16	0.4	0
B	0	99.88	0	0	99.79	0	3.09	69.41	1.85	0

* 0.4 g of Al foil and 50 mmol NaOH was used in 200 mL solution of CH_3OH : H_2O=1:1 (Al was completely dissolved at the end of HDC reaction).

Table S3: Composition of the reaction mixtures obtained by overnight action of 5 mmol $NaBH_4$ and eventually 2 mmol of $CuSO_4$ or $NiSO_4$ on 100 μmol of chlorobenzene (CB) in 200 mL aqueous solution.

Products of HDC	**HDC of chlorobenzene**			
	$CuSO_4/NaBH_4$	**$NiSO_4/NaBH_4$**	**$NaBH_4$**	**Al foil***
CB	100	0.11	95.4	100
B	0	99.89	4.6	0

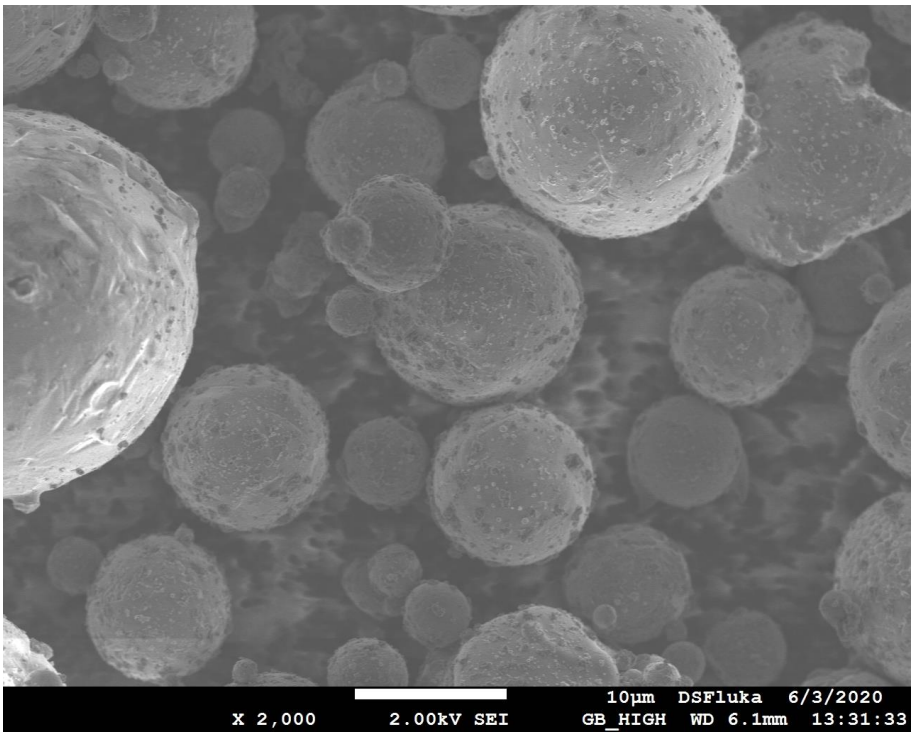
* 0.4 g of Al foil and 50 mmol NaOH was used in 200 mL aqueous solution (Al was completely dissolved at the end of HDC reaction).

SEM of Devardas and Raney Al-Ni alloys used in HDC process

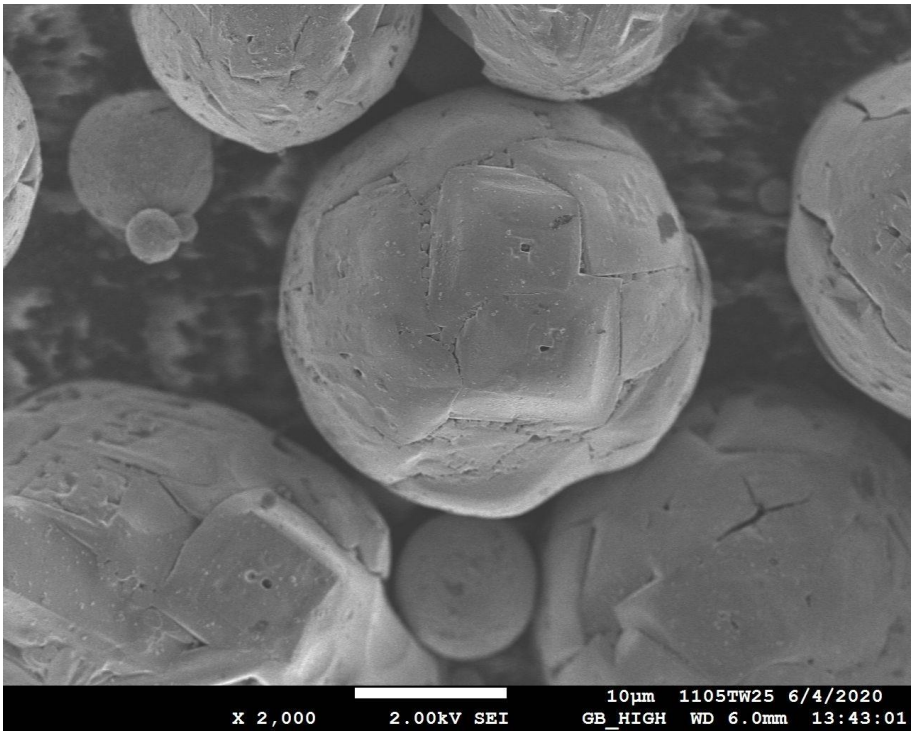
The images of samples were obtained using a scanning electron microscope JEOL JSM-7500F Field Scanning Electron Microscope. Fig. S1 shows the morphology of the fresh and used Devardas alloy particles applied in this study.

Figures S1. SEM images of Devardas Al-Cu-Zn used in HDC process at 2000x magnification for:

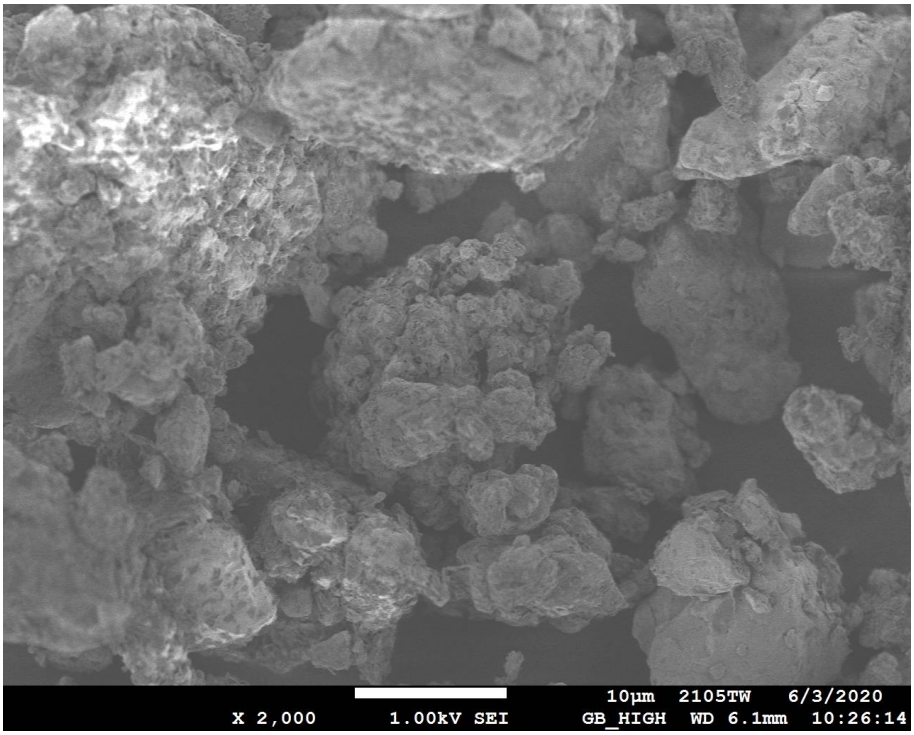
a) Starting Devardas alloy (Fluka)



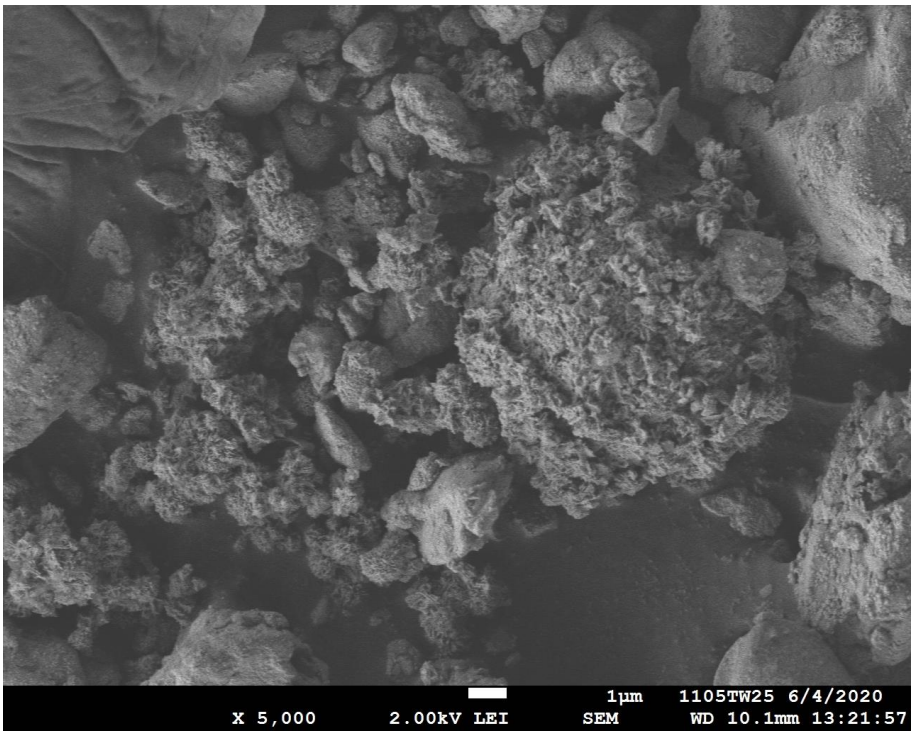
b) used Devardas alloy after 25 min. of the reaction with 1% NaOH in 1:1 H_2O:CH_3OH:



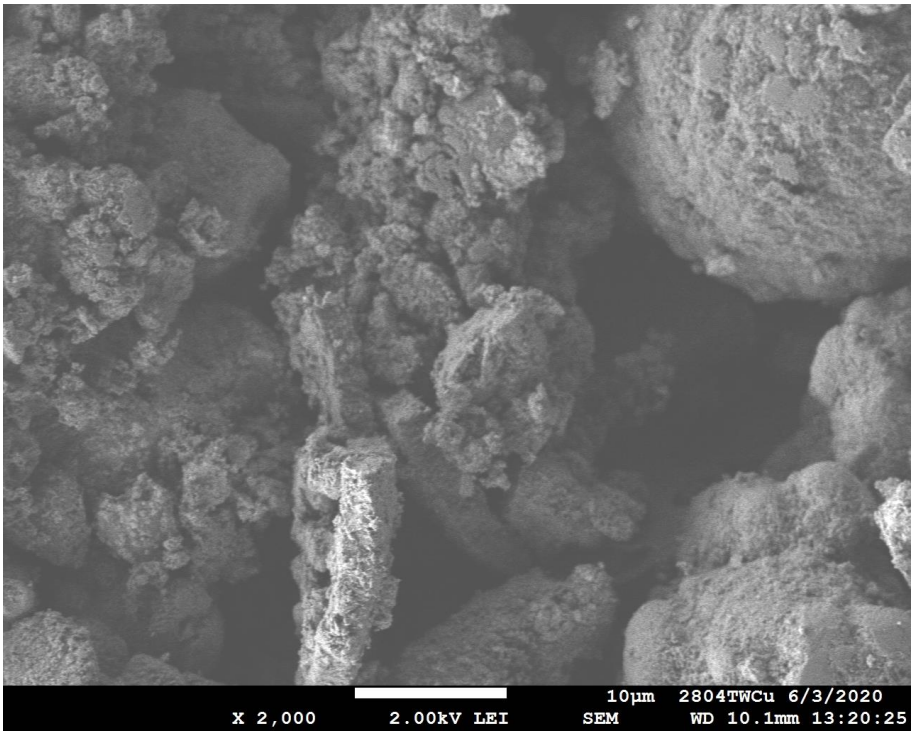
c) Devardas alloy after 40 min. of the reaction with 1% NaOH in 1:1 H_2O : CH_3OH:



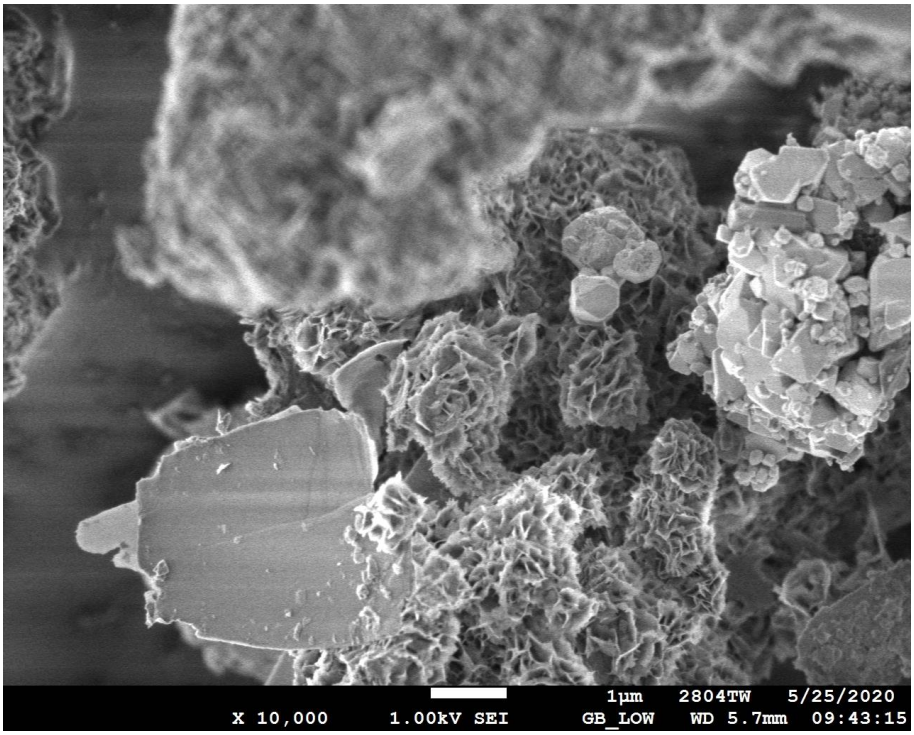
d) Devardas alloy after 60 min. of the reaction with 1% NaOH in 1:1 H_2O : CH_3OH (at 5000x magnification):



e) used Devardas alloy at the end of HDC reaction (after 16 h of the reaction with 1% NaOH in 1:1 H_2O : CH_3OH:

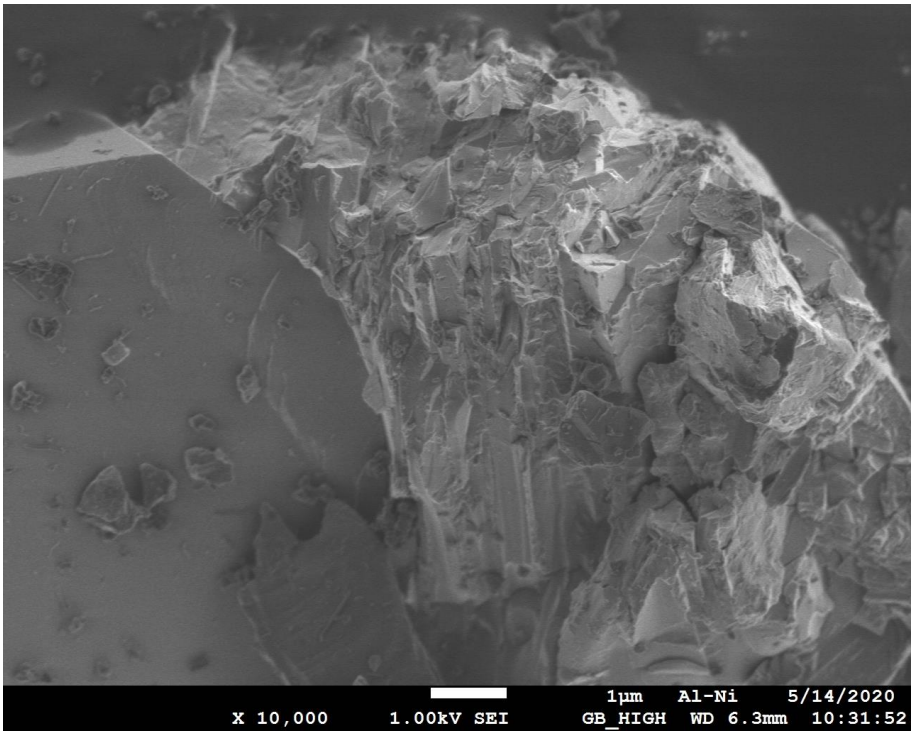


f) used Devardas alloy at the end of HDC reaction (after 16 h of the reaction with 1% NaOH in 1:1 H_2O : CH_3OH (at 10,000x magnification) :

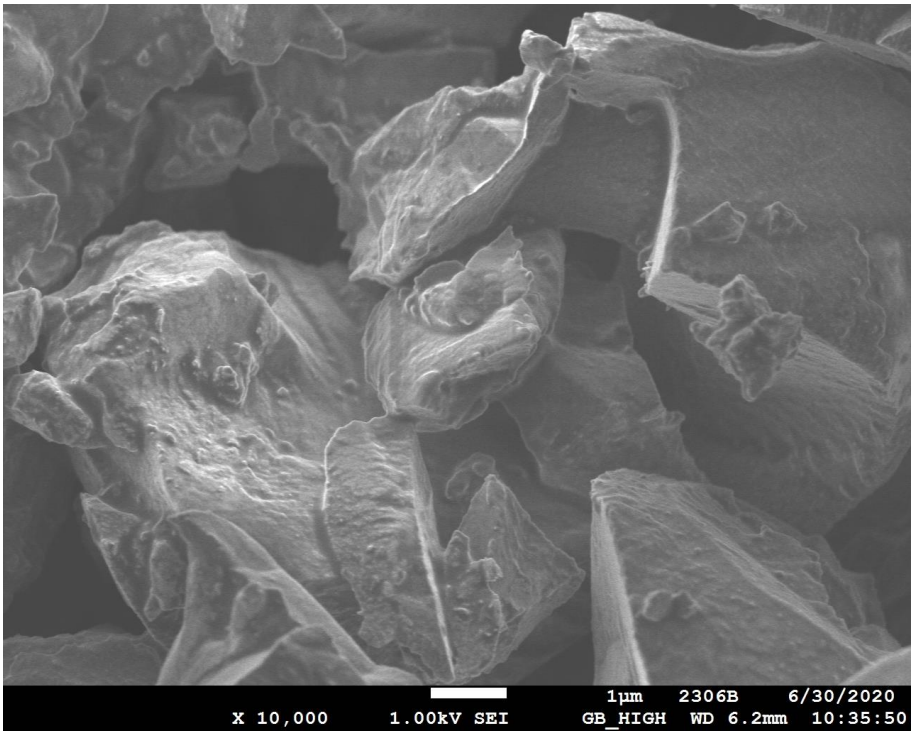


Figures S2. SEM images of Raney Al-Ni alloy used in HDC process at 10,000x magnification for:

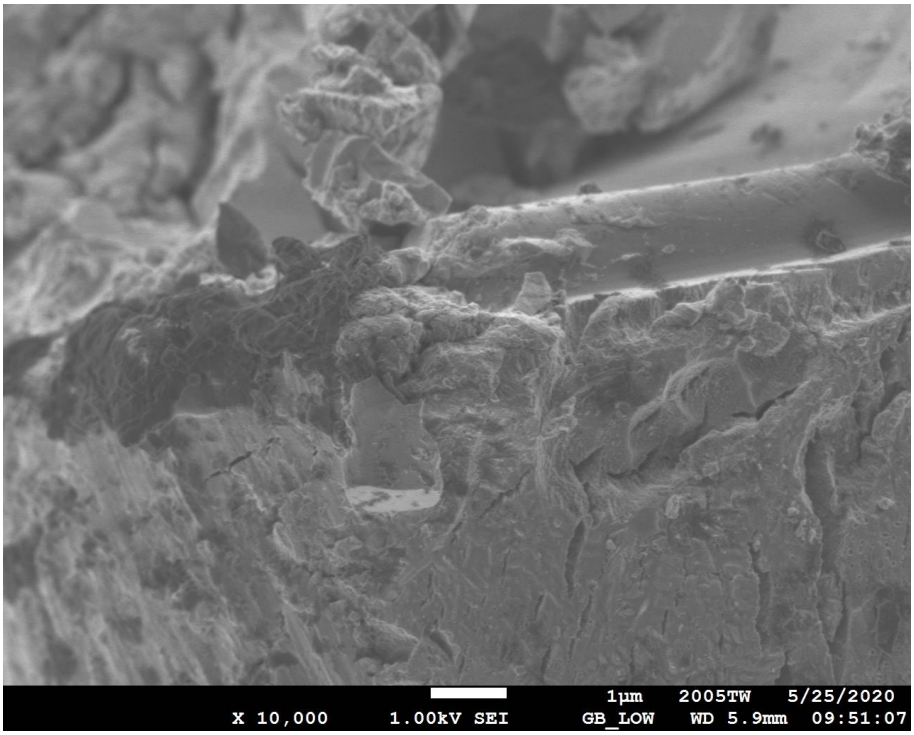
a) Starting Raney Al-Ni alloy



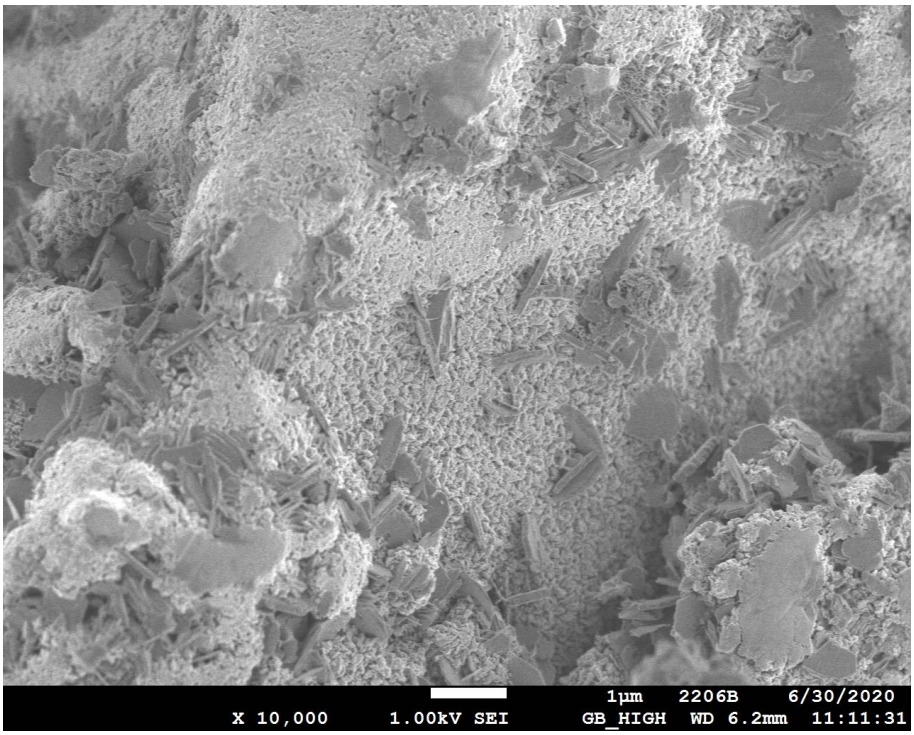
b) Raney Al-Ni alloy after 30 min. of the reaction with 1% NaOH in 1:1 H_2O : CH_3OH (at 10,000x magnification):



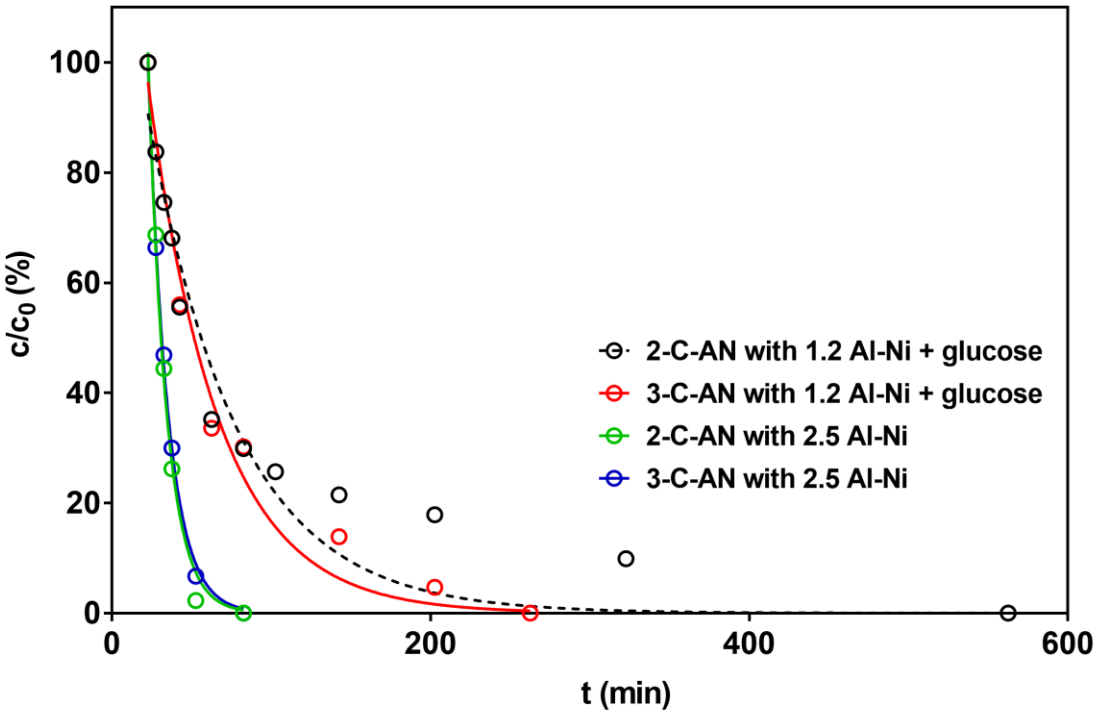
c) Raney Al-Ni alloy after 60 min. of the reaction with 1% NaOH in 1:1 H_2O : CH_3OH (at 10,000x magnification):



d) used Raney Al-Ni alloy at the end of HDC reaction (after 16 h of the reaction with 1% NaOH in 1:1 H_2O : CH_3OH (at 10,000x magnification) :

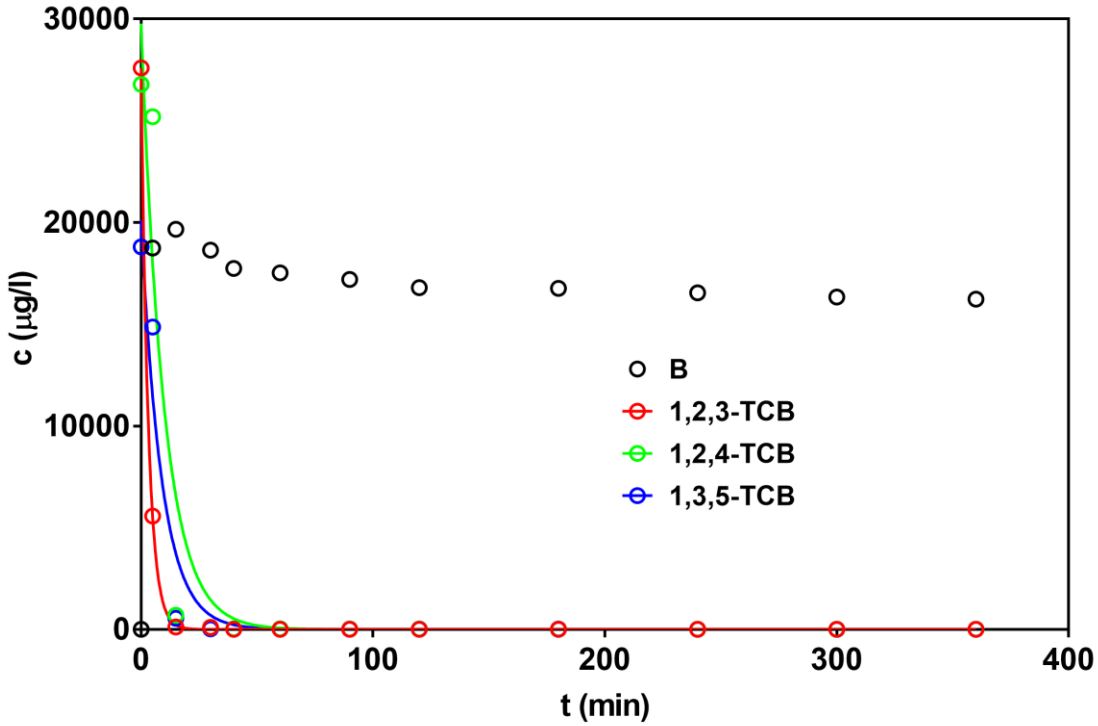


92 **Figure S3**. Time dependences for HDC of Cl-ANs using the Raney Al-Ni alloy with and without
93 addition of glucose, see Ref. [22] for experimental details.



94
95
96

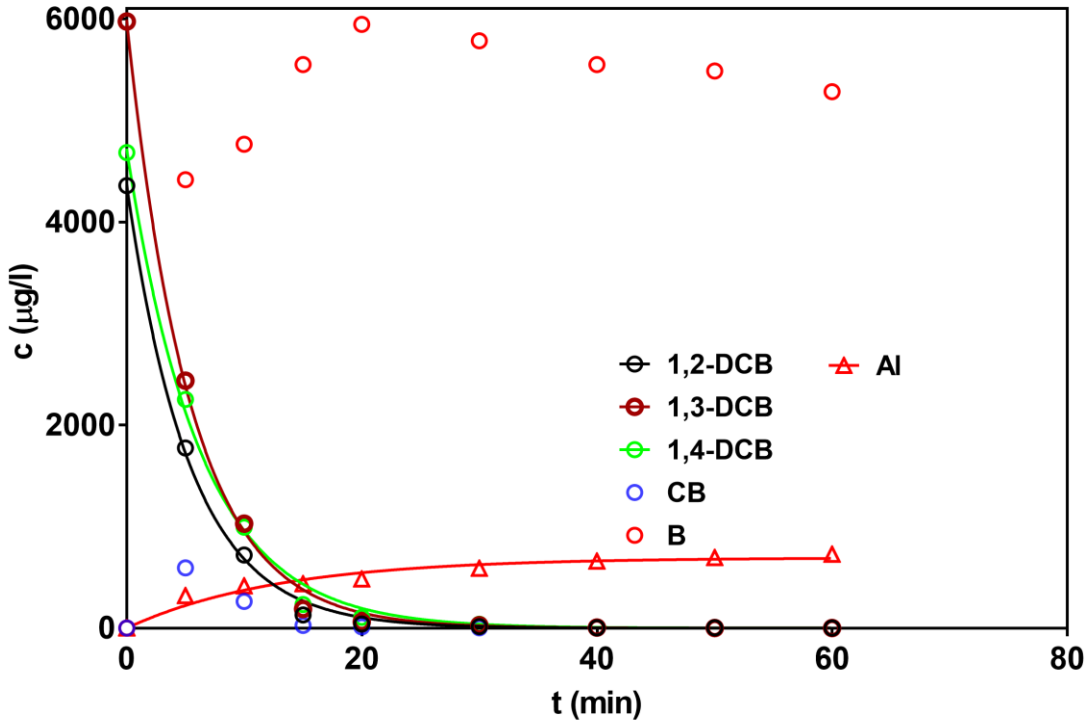
97 **Figure S4**. Time dependences for HDC of triCBs using the Raney Al-Ni alloy.



98

99 Note: When the evolution of hydrogen gas ceases during the HDC, benzene levels slowly began to
100 fall due to its volatile nature.
101

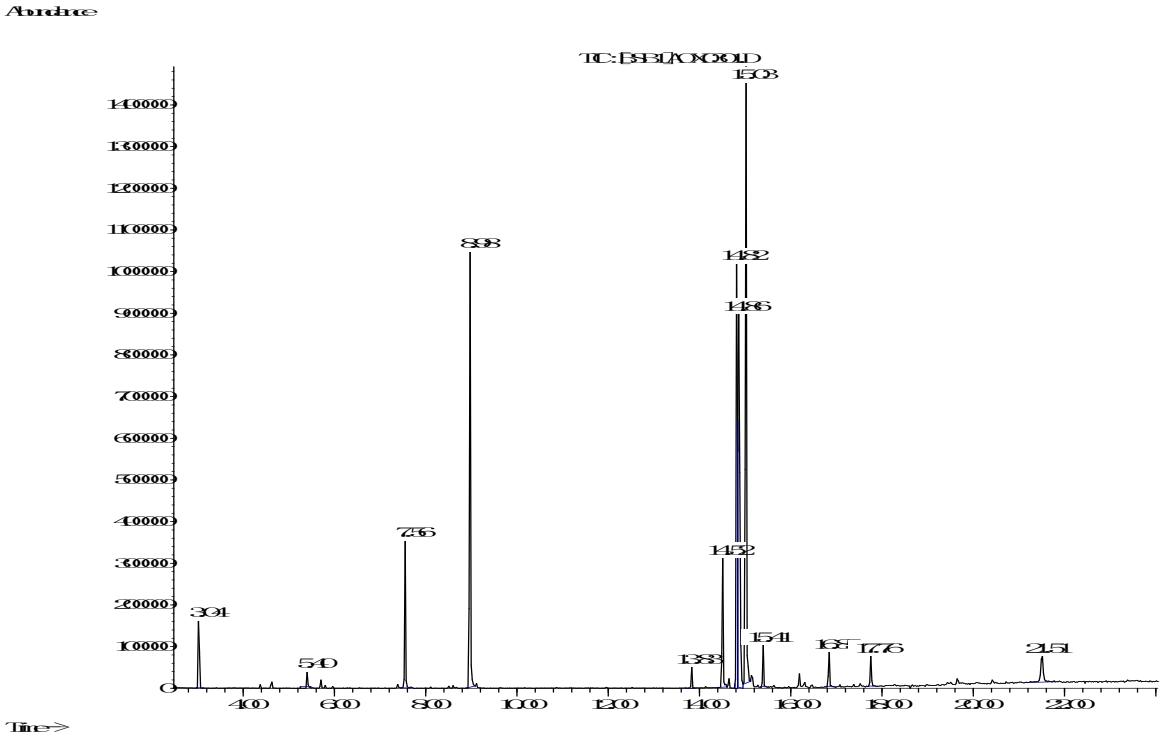
102 **Figure S5**. Time dependences for HDC of DCBs using the Raney Al-Ni alloy.

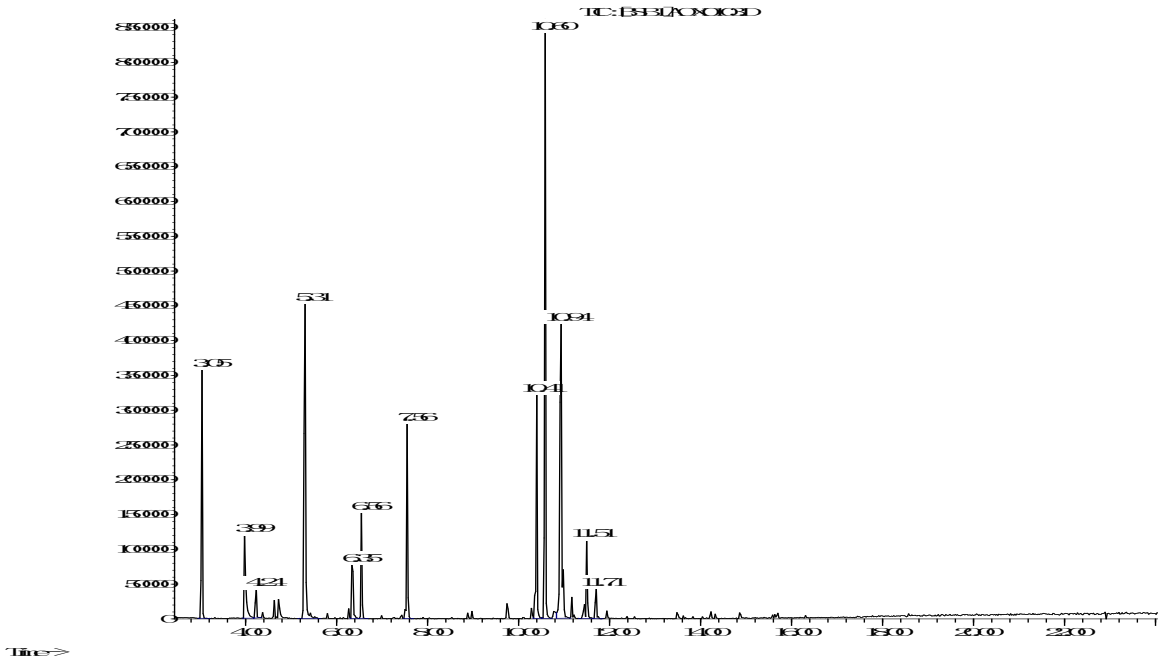


103

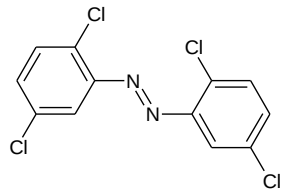
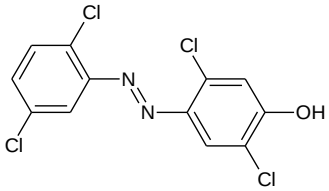
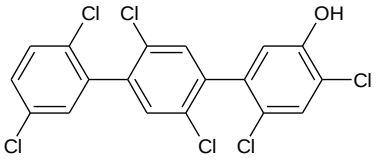
104 Note: We observed that when the evolution of hydrogen gas ceases during the HDC, benzene levels
105 slowly began to fall due to its volatile nature.
106

Figure S6. **a)** GC/MS analysis of DCM extract of **sample 811OVVUOS** (technological water produced at the azo pigments production site)– **upper trace and sample 1112TW** (after HDC treatment) – **bottom trace**.





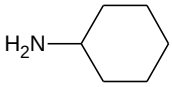
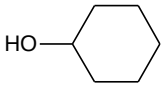
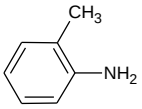
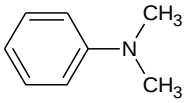
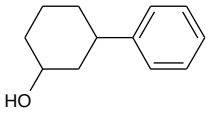
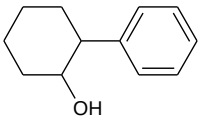
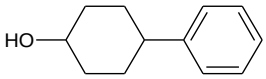
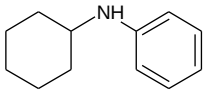
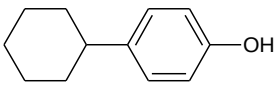
b) ***Qualitative GC/MS analysis of the sample*** **811OVVUOS (**technological water produced at the azo pigments production site)

RT (min)	***MW***	***Structure***
3.04	92	toluene
5.70	146	*m*- + *p*-dichlorobenzene
5.96	146	*o*-dichlorobenzene
7.39	162	dichlorophenol
7.56	***136***	***i.s.***
8.98	161	2,5-dichloraniline
13.83	290	tetrachlorobiphenyl
14.52	272	trichloro-hydroxy-biphenyl
14.82	306	tetrachloro-hydroxy-biphenyl
14.86	***288***	***i.s.***
15.03	306	tetrachloro-hydroxy-biphenyl
15.41, 16.19	305	tetrachloro-amino-biphenyl
16.85	318	
17.76	334	
21.51	450	

Note 1 i.s. internal standard

Note 2 Structures of the detected isomer compounds were not possible confirm due to a lack of corresponding standard compounds

c) Qualitative GC/MS analysis of the sample **1112TW** (after HDC treatment)

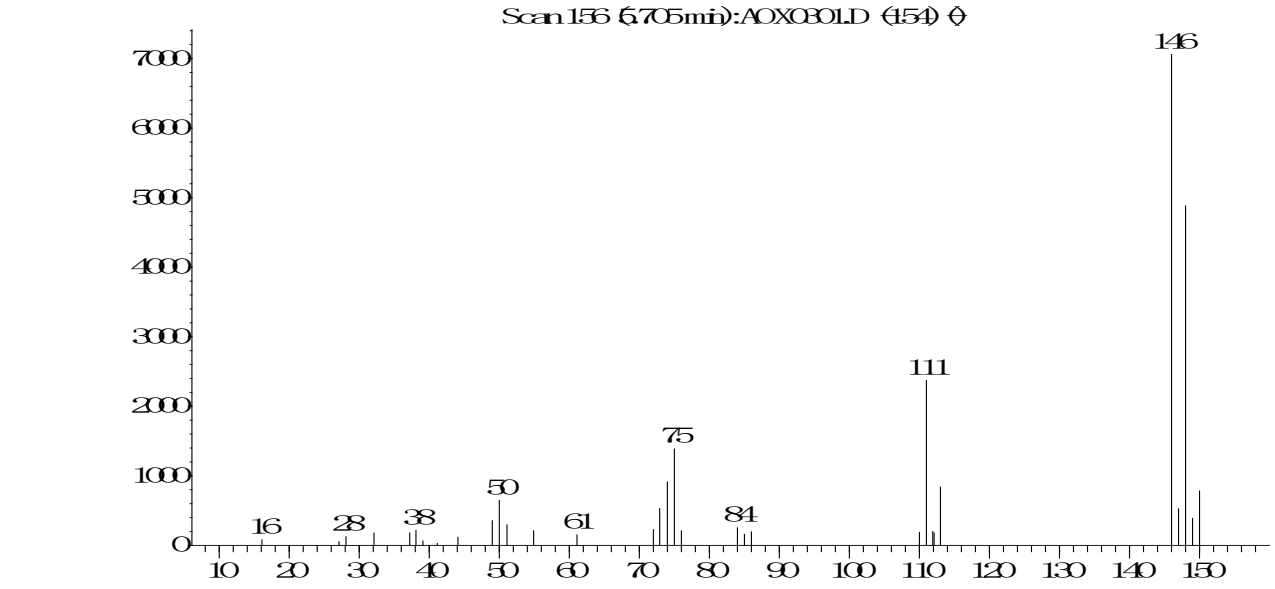
	RT (min)	***MW***	***Structure***
	3.05	92	toluene
	3.99	99	
	4.24	100	
	5.31	93	aniline
	6.35	107	
	6.56	121	
	7.56	**136**	**i.s.**
	10.41	176	
	10.60	176	
	10.94	176	
	10.98	175	
	11.51	176	
	11.71	175	cyclohexylaniline

Note 1 *i.s. internal standard*

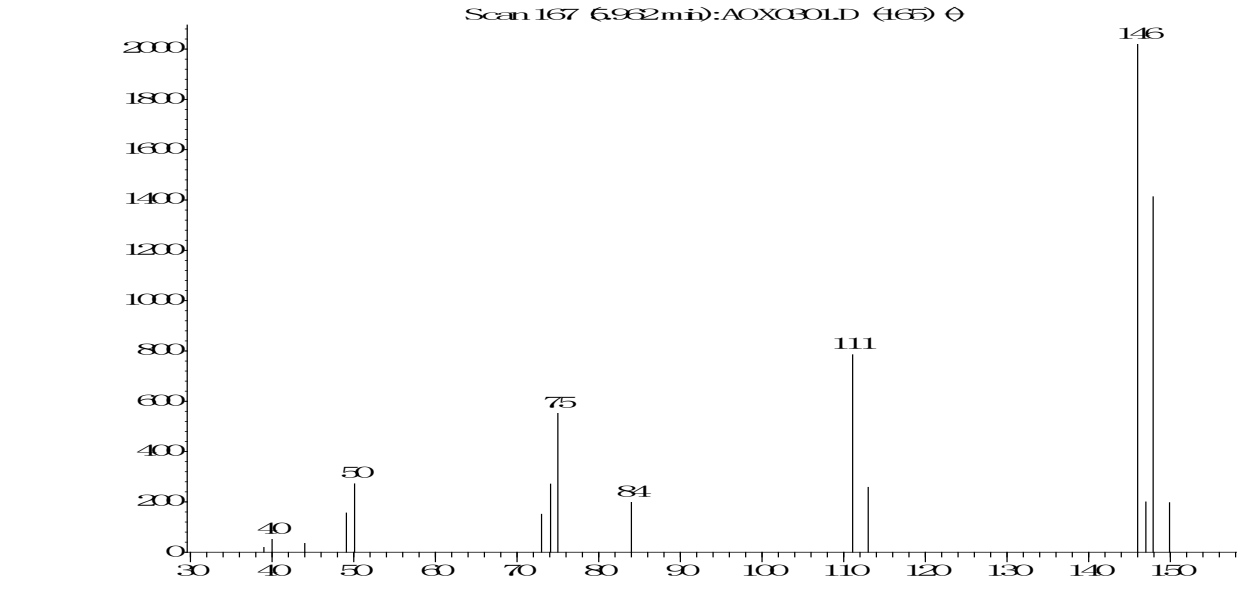
Note 2 *Structures of the detected isomer compounds were not possible confirm due to a lack of corresponding standard compounds*

d) MS spectra of chlorinated aromatic compounds identified in the sample 811OVVUOS (technological water produced at the azo pigments production site):

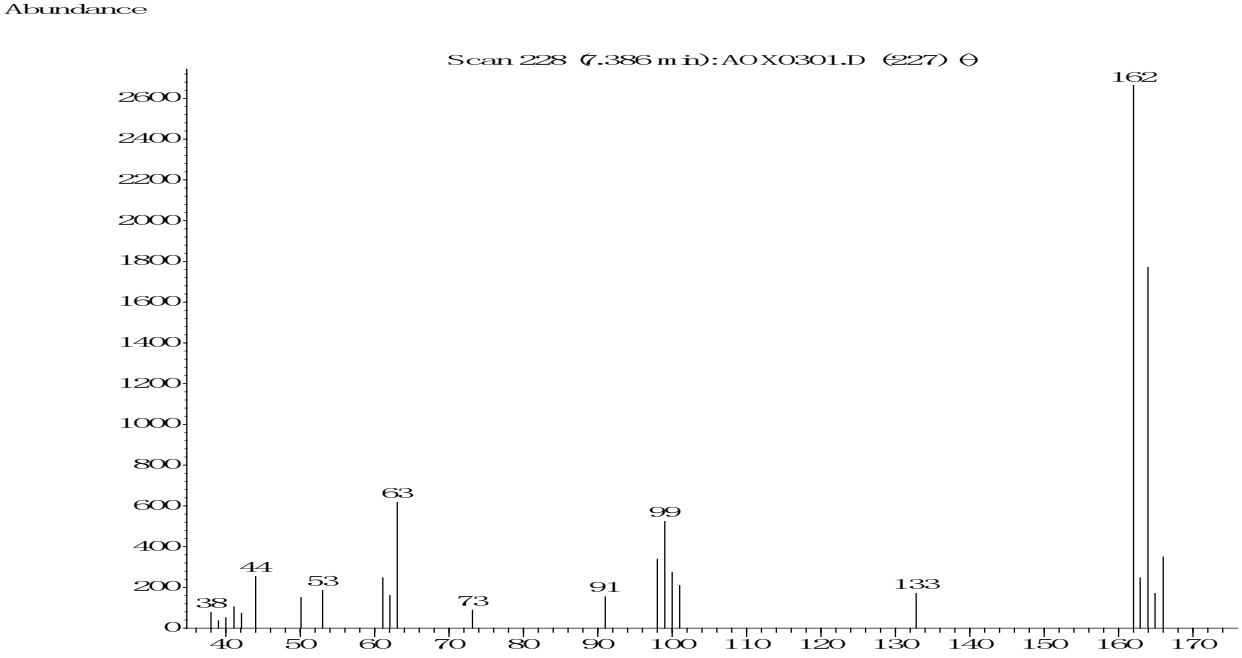
Mass spectrum (EI, 70 eV) of m+p-dichlorobenzene (RT=5.70 min):



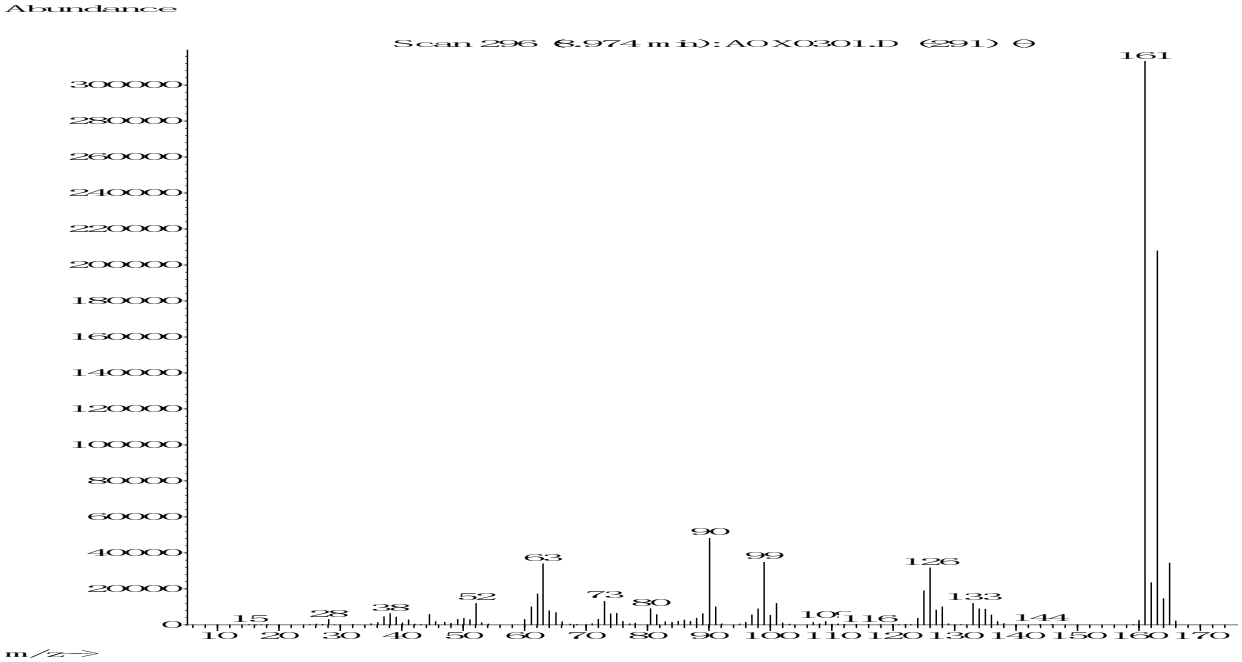
Mass spectrum (EI, 70 eV) of o-dichlorobenzene (RT=5.96 min):



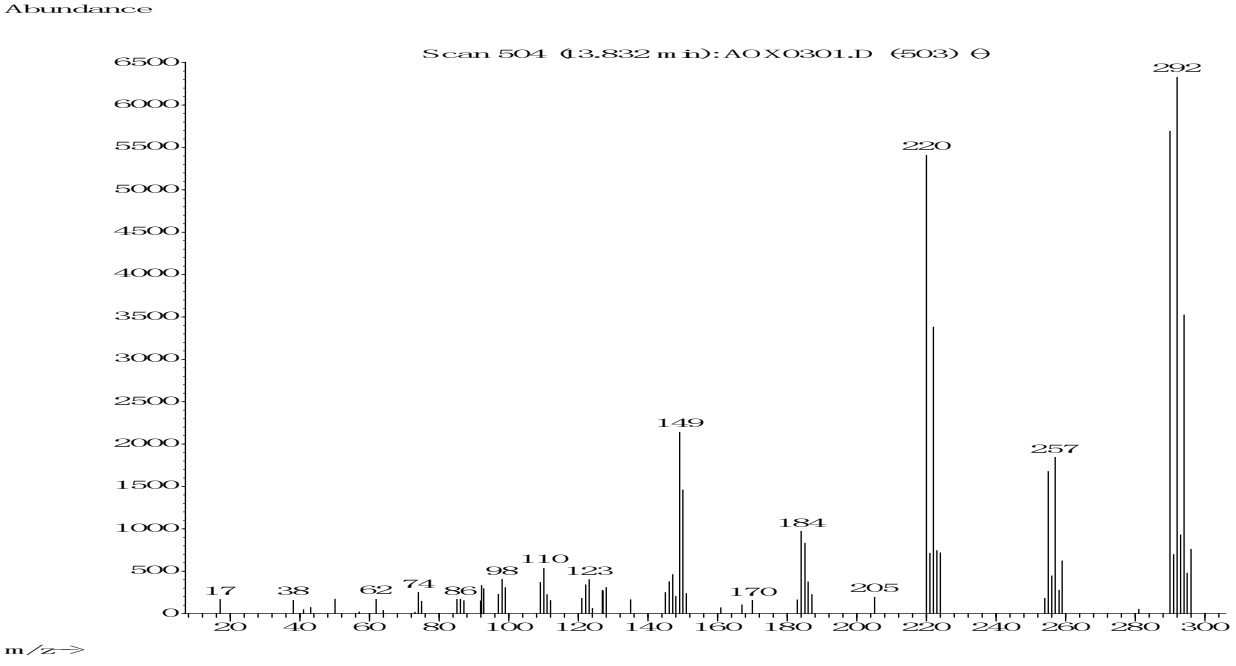
Mass spectrum (EI, 70 eV) of dichlorophenol (RT=7.39 min):



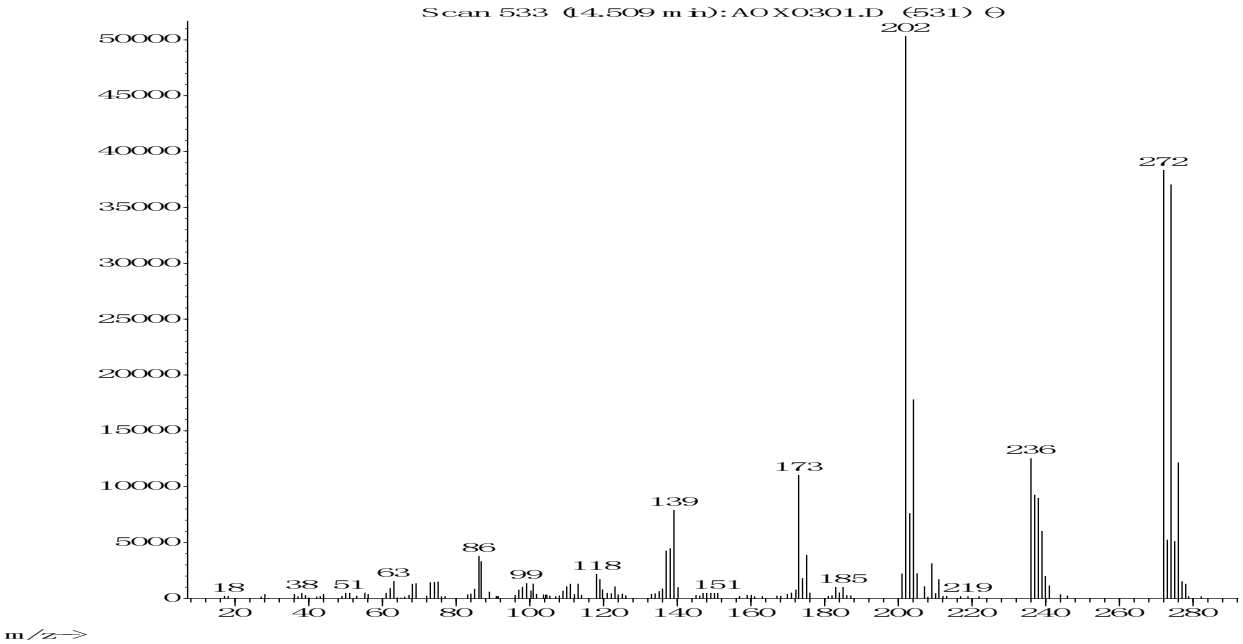
Mass spectrum (EI, 70 eV) of 2,5-dichloroaniline (RT=8.97 min):



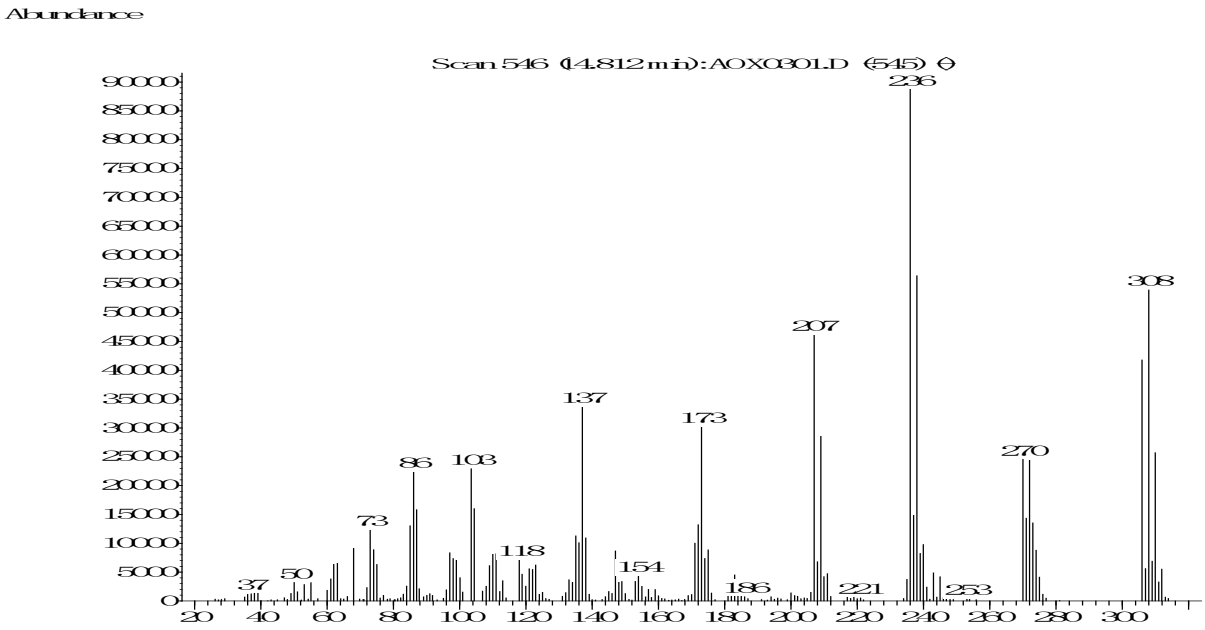
Mass spectrum (EI, 70 eV) of tetrachlorobiphenyl (RT=13.83 min):



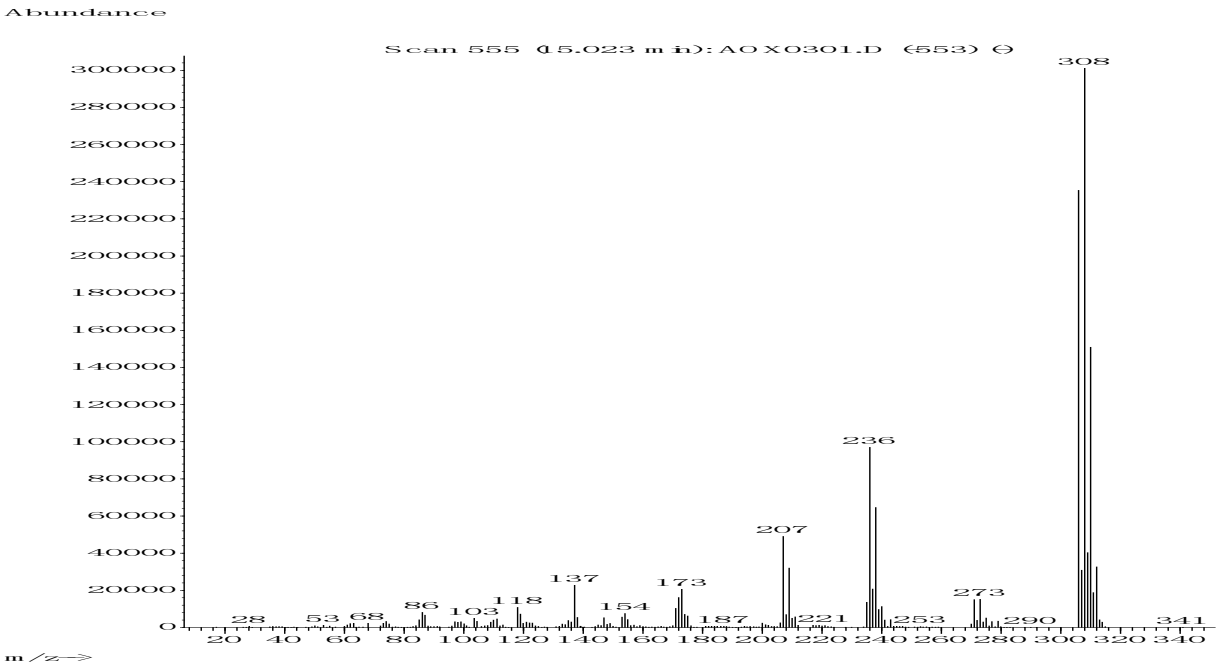
Mass spectrum (EI, 70 eV) of trichloro-hydroxy-biphenyl (RT=14.52 min):



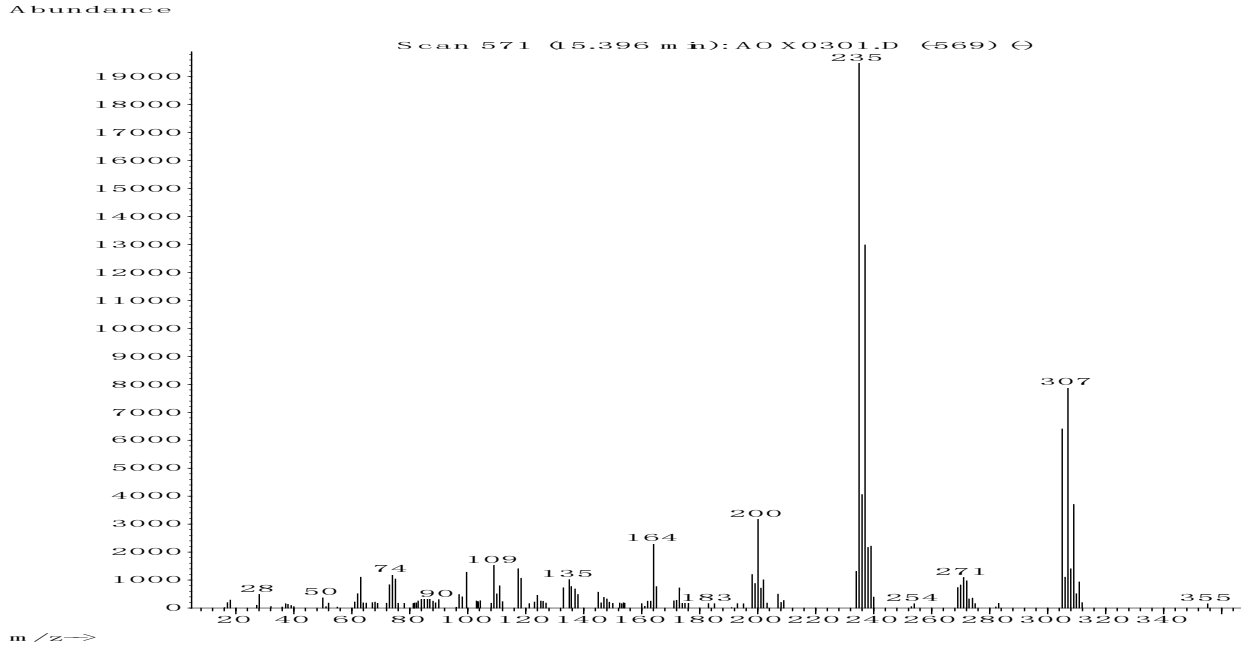
Mass spectrum (EI, 70 eV) of tetrachloro-hydroxy-biphenyl (RT=14.82 min):



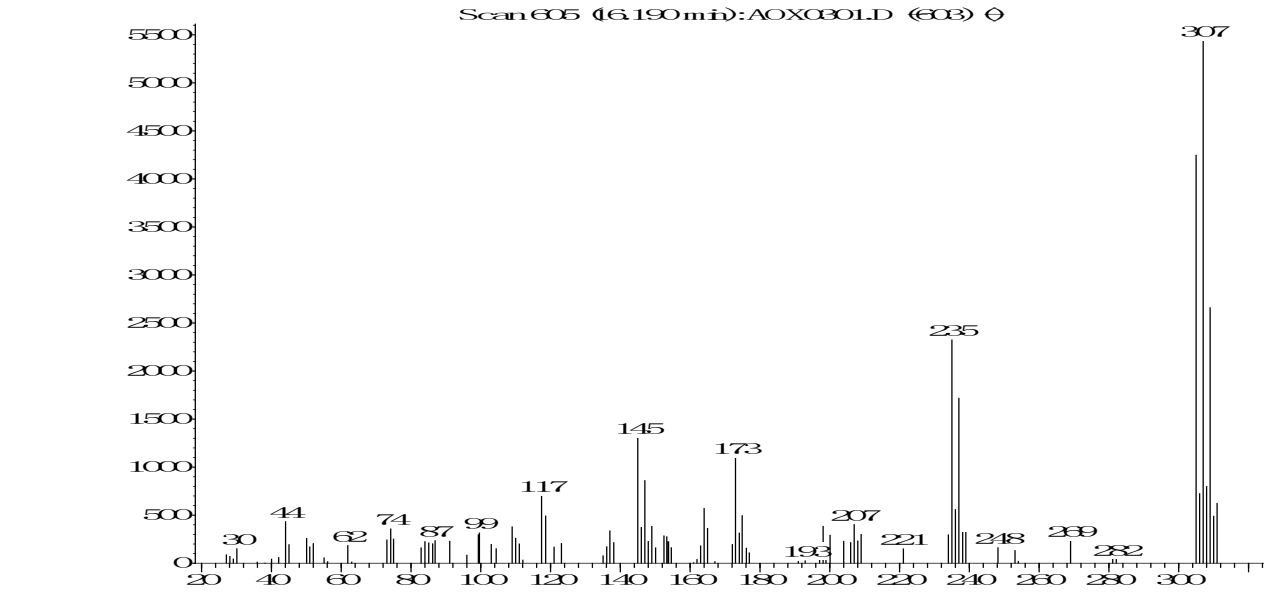
Mass spectrum (EI, 70 eV) of tetrachloro-hydroxy-biphenyl (RT=15.03 min):



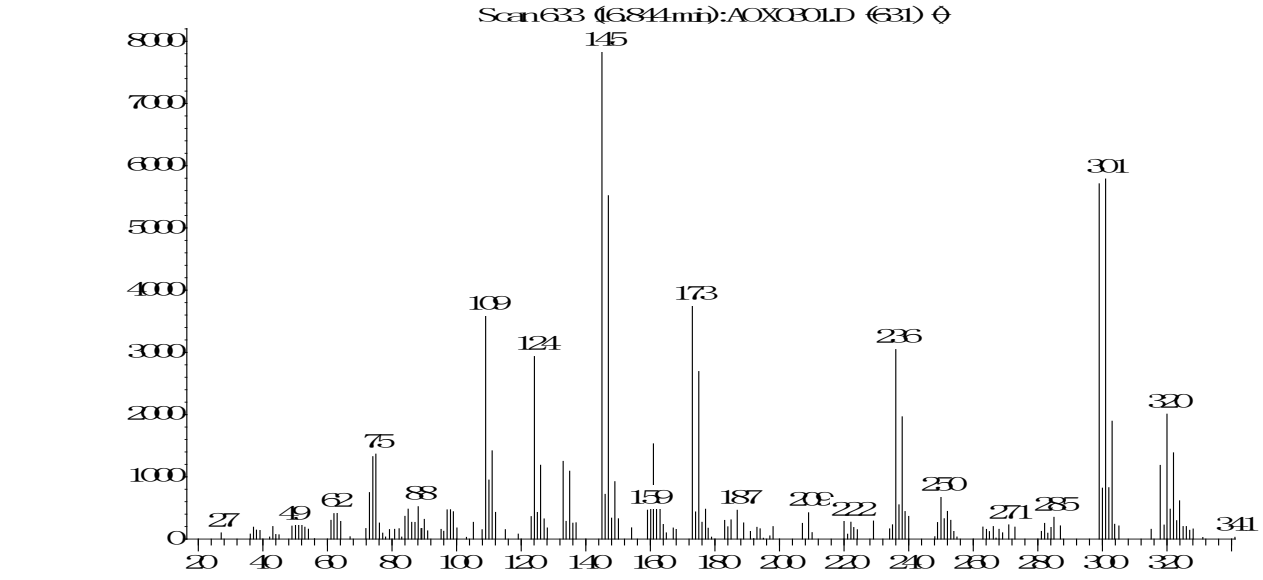
Mass spectrum (EI, 70 eV) of tetrachloro-amino-biphenyl (RT=15.41 min):



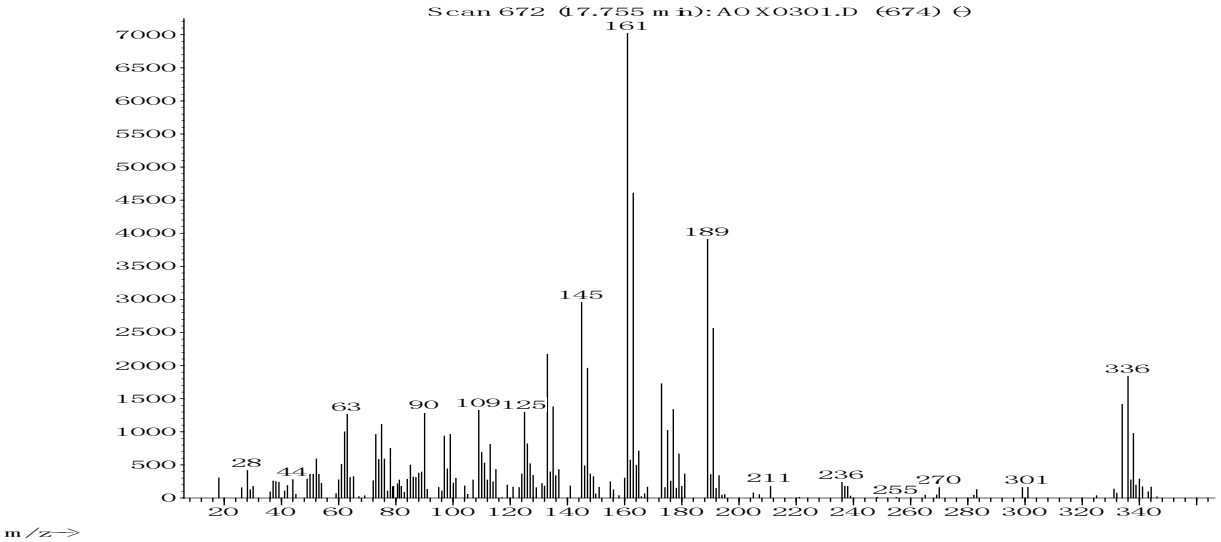
Mass spectrum (EI, 70 eV) of tetrachloro-amino-biphenyl (RT=16.19 min):



Mass spectrum (EI, 70 eV) of tetrachloro-azobenzene (RT=16.85 min):

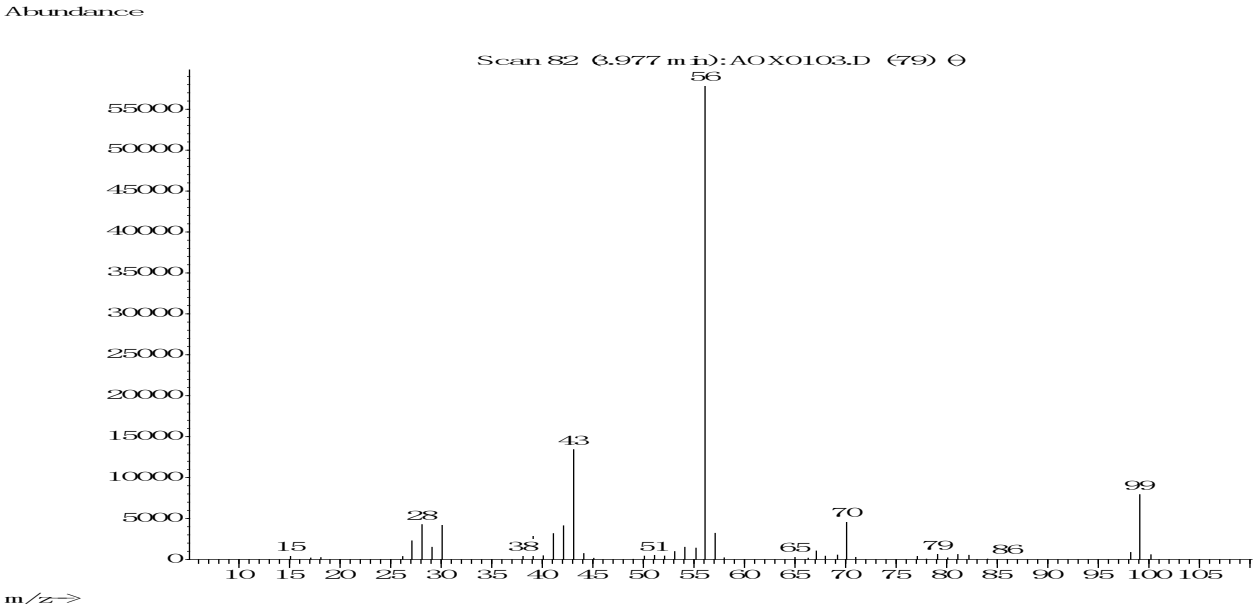


Mass spectrum (EI, 70 eV) of tetrachloro-hydroxy-azobenzene (RT=17.76 min)

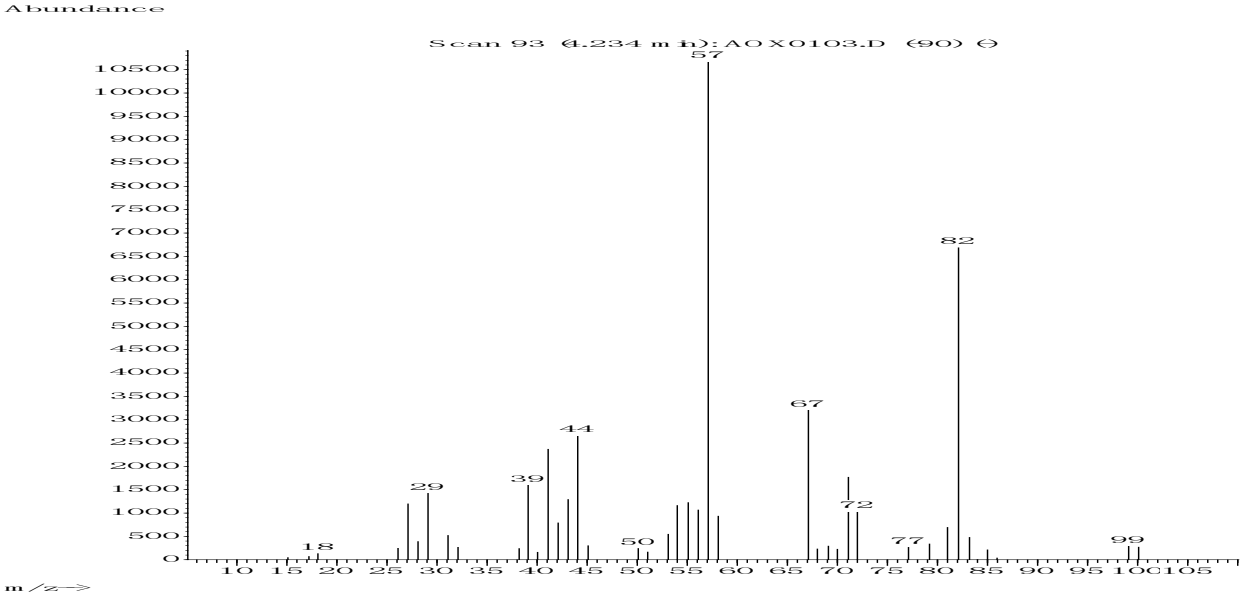


e) MS spectra of products obtained after HDC of chlorinated aromatic compounds in 811OVVUOS sample (**identified in sample 1112TW**):

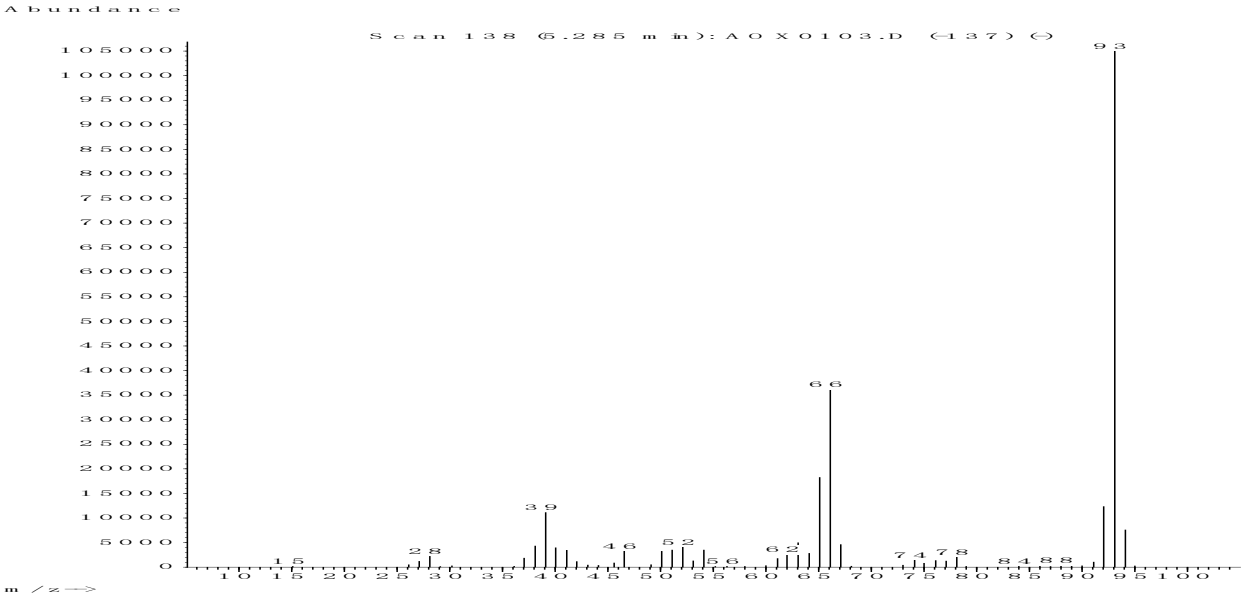
Mass spectrum (EI, 70 eV) of cyclohexylamine (RT=3.99 min):



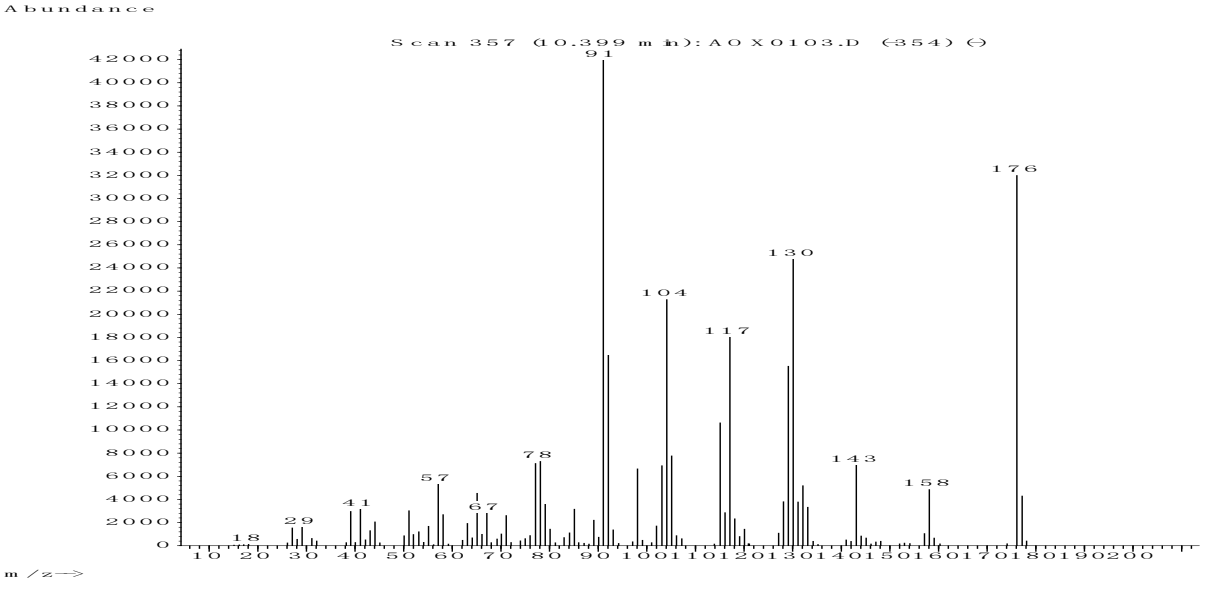
Mass spectrum (EI, 70 eV) of cyclohexanol (RT=4.24 min):



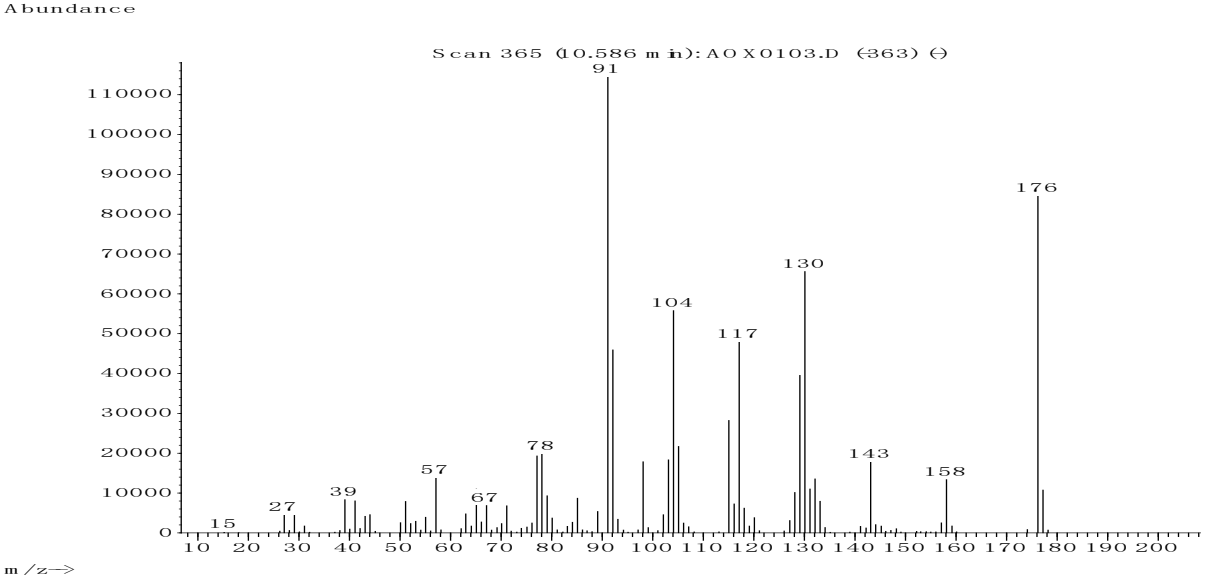
Mass spectrum (EI, 70 eV) of aniline (RT=5.31 min):



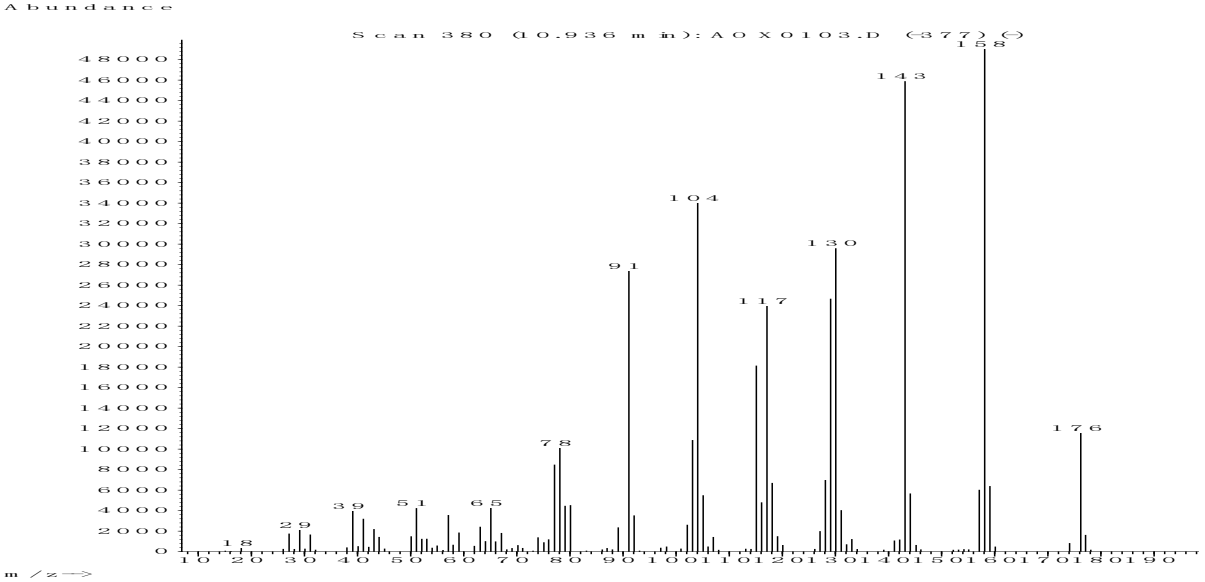
Mass spectrum (EI, 70 eV) of phenylcyclohexanol (RT=10.41 min):



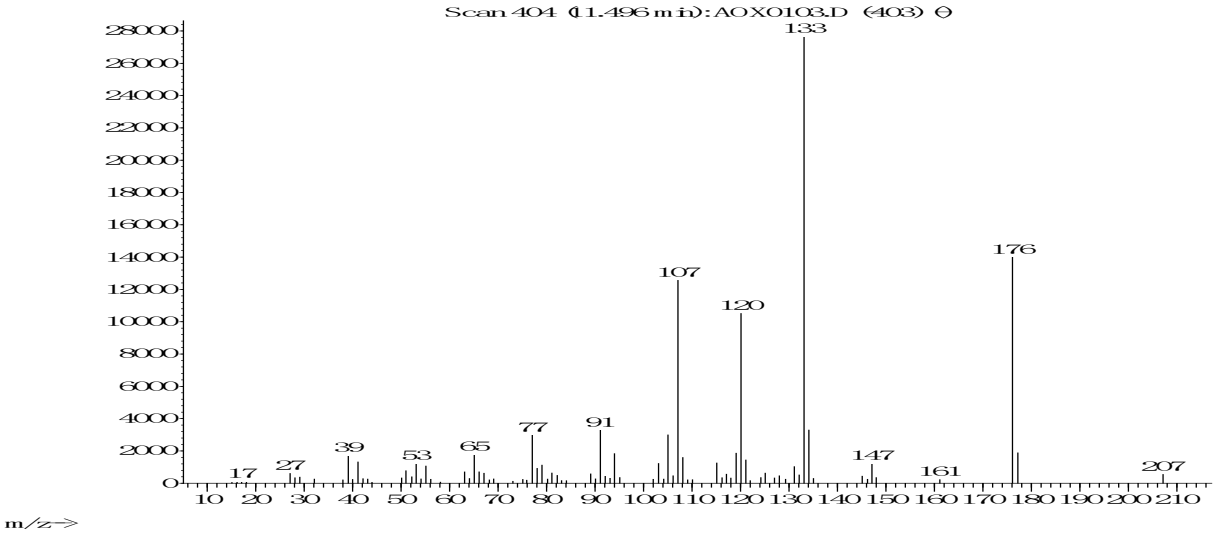
Mass spectrum (EI, 70 eV) of phenylcyclohexanol (RT=10.60 min):



Mass spectrum (EI, 70 eV) of phenylcyclohexanol (RT=10.94 min):



Mass spectrum (EI, 70 eV) of cyclohexylphenol (RT=11.51 min):



Mass spectrum (EI, 70 eV) of cyclohexylaniline (RT=11.71 min):