Analysis of epoxy anti-corrosion coatings with (reactive) pyrolysis gas chromatography/mass spectrometry

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Introduction

Marine coatings, specifically anti-corrosion or antifouling paints, could be the largest source of microplastics in the marine environment, according to new estimates[1]. However, there is very little environmental data on marine paint particles. One of the reasons is the analytical challenge posed by the heterogeneous composition, density, and structural complexity of these organic coatings.

Epoxy resins (EP) are one of the major anti-corrosion coating types used in the marine environment. Therefore, we are investigating the potential of pyrolysis gas chromatography/mass spectrometry (Py-GC/MS)

- to identify EP
- to distinguish them from structurally similar poly-carbonate (PC)
- to achieve mass quantification

Table 1: Direct pyrolysis and reactive pyrolysis targets for 3 different EP products from different manufacturers (product A, B, C) and a PC reference product.

Peak #	Compound	BP [m/z]	RI	direct pyrolysis Prod. A	Prod. B	Prod. C	PC	reactive pyrolysis Prod. A	Prod. B	Prod. C	PC
1	Benzene	78	681								
2	**Toluene**	91	767								
3	non-identified compound	109	786								
4	*p*-Fluoroethylbenzene	109	880								
5	Anisole	77	920								
6	**2-Ethylhexanal**	72	958								
7	3-Ethyltoluene	105	972								
8	Phenol	94	987								
9	1-Fluoro-4-(1-methylethenyl)benzene	136	991								
10	*Methoxymethylbenzene*	91	995								
11	Benzofuran	118	1001								
12	2-Methylanisole	122	1014								
13	2-Ethyl-1-hexanol	117	1034								
14	*o*-Cresol	108	1060								
15	**1-Methyl-4-isopropylbenzene**	132	1096								
16	Methyl benzoate	105	1102								
17	2-Methylbenzofuran	131	1115								
18	**2-Ethylphenol**	107	1143								
19	2-Isopropylbenzaldehyde	*148*	*1172*								
20	**3-Ethylphenol**	107	1173								
21	***o*-Isopropylanisole**	135	1182								
22	*p*-Isopropylphenol	119	1237								
23	2-Allyl-4-methylphenol	77	1252								
24	*p*-isopropenylphenol	121	1311								
25	1,3-Bis(1-methylethenyl)benzene	158	1331								
26	non-identified compound	162	1339								
27	non-identified compound	*159*	*1387*								
28	non-identified compound	172	1452								
29	Dibenzofuran	168	1540								
30	1,2-Difluoro-1,2-diphenylethane	109	1554								
31	1-Fluoro-4-(1,3-dimethyl-3-butenyl)benzene	123	1584								
32	Ethyl laurate	88	1597								
33	9H-Xanthene	182	1664								
34	1,3-Diisopropylnaphthalene	197	1692								
35	2,6-Diisopropylnaphthalene	197	1698								
36	2,3-Dihydro-1,1,3-trimethyl-1H-indene	221	1745								
37	3,3',4,4'-Tetramethylbiphenyl	210	1759								
38	non-identified compound	135	1772								
39	2-Methoxydibenzofuran	198	1791								
40	1-Chloro-2-methyl-2-phenylpropane	119	1818								
41	1-Methoxy-4-(2-phenylpropan-2-yl)benzene	211	1829								
42	2,4-Diphenyl-4-methyl-2(E)-pentene	143	1858								
43	2,4,6-Trimethyl1,1'-biphenyl	196	1871								
44	4-(1-Methyl-1-phenylethyl)-phenol	197	1893								
45	1-Methoxy-2-((4-methoxyphenyl)methyl)benzene	228	1863								
46	non-identified compound	148	1900								
47	4,4'-Dimethoxydiphenylmethan	228	1924								
48	2,6-Di-tert-butylnaphthalene	225	1933								
49	2-(4'-Methoxyphenyl)-2-(2'-methoxyphenyl)propane	241	1953								
50	Dimethylbisphenol F	197	1989								
51	Dimethylbisphenol A	241	2097								
52	2-(4'-Methoxyphenyl)-2-(3'-methyl-4'methoxyphenyl)propane	255	2143								
53	*4-[1-(4-Methoxyphenyl)-1-methylethyl]phenol*	227	2155								
54	**Methyl 3,5-di-tert-butyl-4-hydroxybenzoate**	249	2161								
55	**Bis(4-tert-butylphenyl) ether**	267	2289								
56	non-identified compound	281	2249								
57	**9-Ethyl-3,6-dimethoxy-10-methylphenanthrene**	265	2327								

Compound detected in each measurement
Compound detected in some measurements
Compound not detected in measurement

Materials and Methods

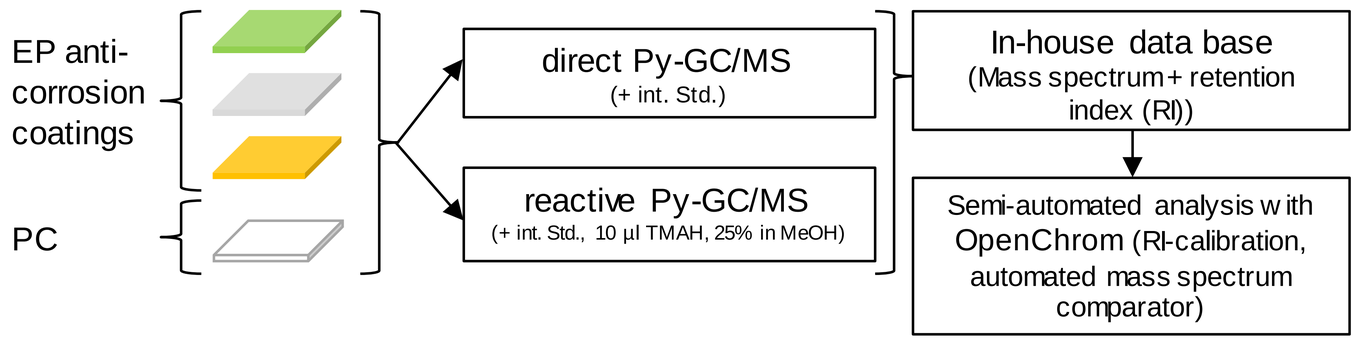

Figure 1: Schematic procedure of the analyses.

Identification

- A total of 55 compounds were identified for the different EP products (Table 1 & Figure 2; direct pyrolysis 36 compounds; reactive pyrolysis 53 compounds)
- Direct Py-GC/MS detected 26 compounds present in each measurement of each product; reactive Py-GC/MS: 28 compounds
- Of these compounds, 9 were not detected for PC (Table 1, in bold), 2 compounds were only identified for PC (italics)

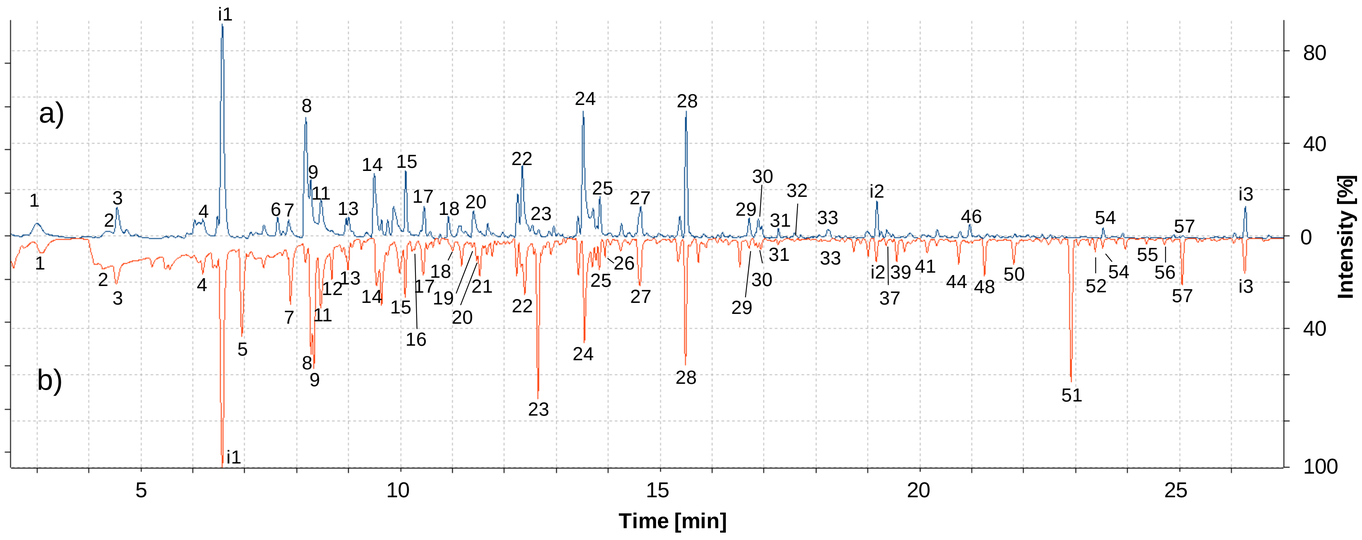

Figure 2: Pyrograms of epoxy resin (product B) obtained by a) direct pyrolysis; b) reactive pyrolysis with TMAH.

Quantification

- Linear correlations over wide calibration ranges for multiple pyrolysis products
- For most compounds: Product A & B very similar in response, product C with small offset
- PC fits into product A & B calibration curve (exception Dimethylbisphenol A)

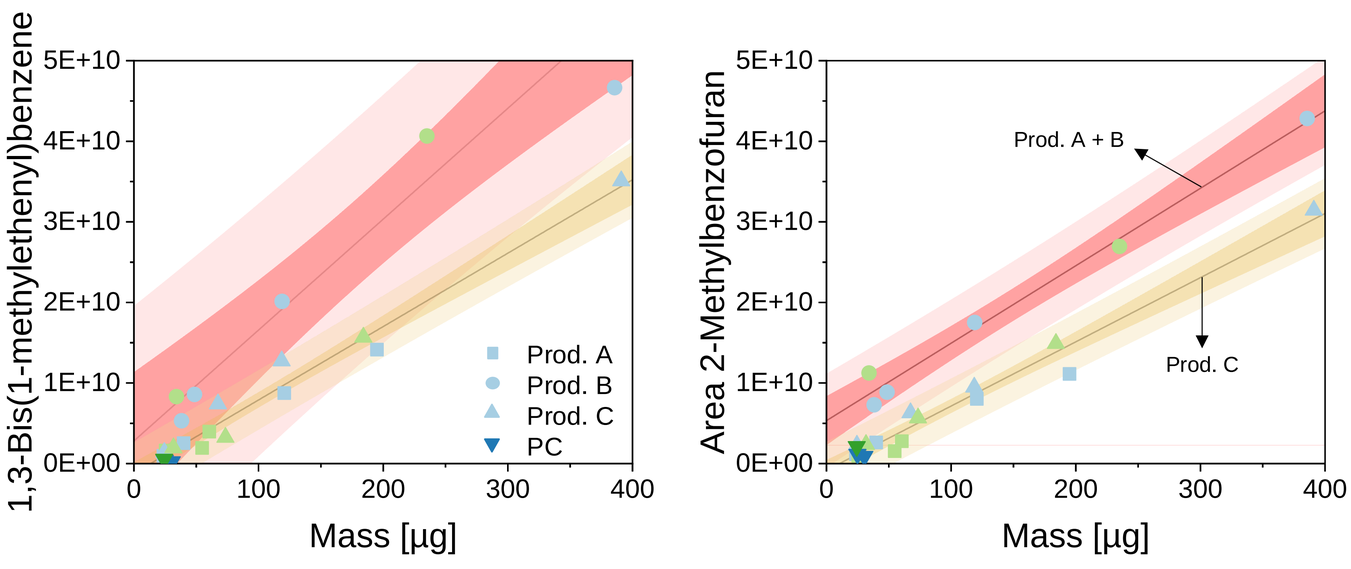

Figure 3: Examples of calibration curves for EP; blue symbols = direct Py-GC/MS, green symbols = reactive Py-GC/MS.

Outlook

- Expansion of the data basis for EP and especially PC (more products, weathered coatings); Influence of catalytic effects
- Application to marine sediments

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Literature

[1]Paruta, P., Pucino, M., & Boucher, J. (2022). *Plastic Paints the Environment*. https://www.e-a.earth/_files/ugd/425198_a864877fefd74ade85d85080ae21e029.pdf