Identification of Potential Pollutants in Road Marking Paints Using Multiple MS Techniques

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Abstract

Road marking paints are a major source of road dust, which can pollute soil and aquatic ecosystems near roads. This study used multiple mass spectrometry techniques to identify potential pollutants in road marking paints. Volatile chemicals were analyzed using pyrolysis GC-MS, while the ethanol-extractable fraction of chemicals was analyzed using LC-MS and GC-MS.

We found 28 unique chemicals in road marking paints, including plasticizers, UV stabilizers, monomers, and surfactants. Most of these chemicals were classified as non-toxic or weak irritants. However, some chemicals, such as dicyclohexyl phthalate, *o*-anisidine, *m*-anisidine, isophorone diisocyanate, and isobornyl acrylate, have significant hazardous properties, including carcinogenicity, reproductive toxicity, respiratory toxicity, and aquatic toxicity.

The presence of these hazardous chemicals in road marking paints highlights their potential to contribute to the environmental impact of road marking paint pollution. This study emphasizes the importance of understanding the composition of road marking paints and their associated hazards to develop effective strategies for mitigating environmental contamination caused by road dust.

Introduction

- Road marking paints are estimated to contribute up to 10%.
- Road marking paint particles have been detected in soils near highways and river sediments.
- Road marking paints contain various organic additives that can pollute the environment, but information about their chemistry and toxicity is limited.
- This study aims to identify the organic additives in road marking paint particles and to present the known hazardous properties of each additive.

Experimental

1. Sample Information

KS M 6080 TYPE 2 Waterborne paints — White, Yellow

KS M 6080 TYPE 5 Cold plastic paints — White, Yellow

2-W 2-Y 5-W 5-Y

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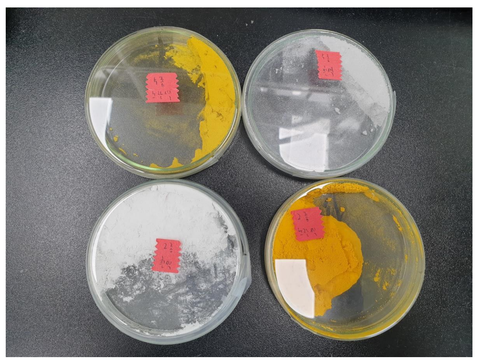
Cryomilling (SPEX 6875A)

→ Paint particles



2. Sample Analysis

Particle

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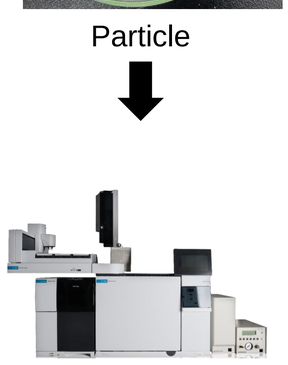
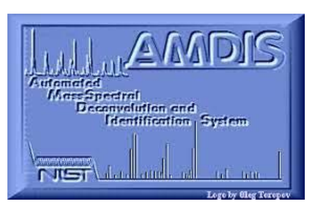
Pyrolysis GC/MS (EI)



Mass spectral library matching



Ethanol extraction

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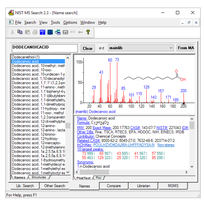
LC/MS/MS (ESI)

GC/MS (EI)

Identification & toxicity assessment

- NIST probability (>70%)
- Manual inspection of the library spectrum match
- Compounds listed in PubChem and ECHA with known toxicity or known usage as plastic additives



Results

1. Chromatographic similarity between the samples

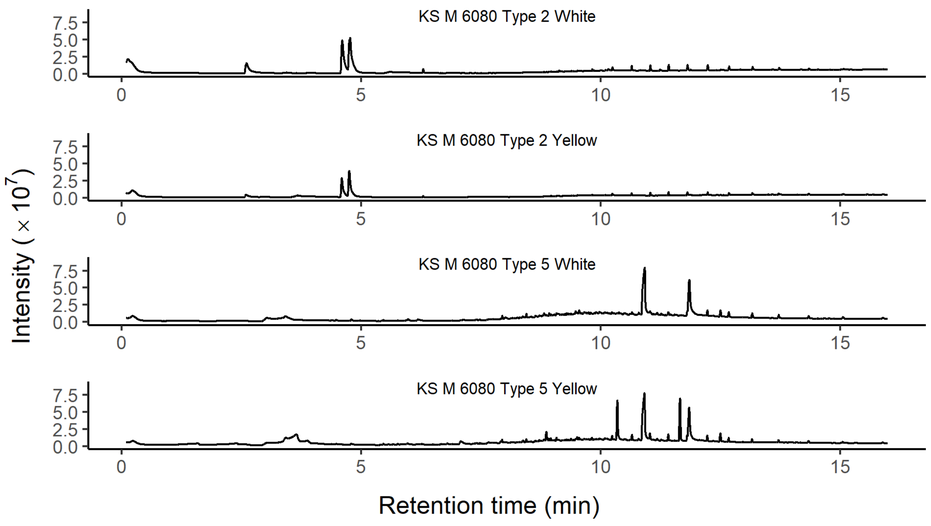


Figure 1. Total ion chromatograms of four paint samples analyzed using py-GC/MS.

- Paints of the same type had similar chromatograms in py-GC/MS, indicating that the organic additives in the paints differ based on the paint type.
- Type 5 yellow paint showed two significant peaks that were not found in type 5 white paint. These peaks were identified as phthalates, but with a low NIST probability.
- At 10-15 minutes retention time, a small series of peaks appeared. These peaks are suspected to be binder polymer peaks.

2. List of identified organic additives in the paints

Table 1. List of known plastic additives and toxic chemicals putatively identified in the MS analysis. The last four columns indicate whether the chemical was present ('O') or absent ('X') in the corresponding paint.

Name	Known toxicity	Known functions	Instrument	2-W	2-Y	5-W	5-Y
1-Methoxy-2-propyl acetate	None	Paint solvent	GC/MS	X	X	X	O
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	Reproductive toxicity, Aquatic toxicity	Plasticizer	GC/MS	O	O	X	X
Butanal	None	Reaction intermediate	GC/MS	O	X	X	X
Dicyclohexyl phthalate	Strong reproductive toxicity, Aquatic toxicity	Plasticizer	GC/MS	X	X	O	O
2,4-Dihydroxybenzophenone	Skin irritant, Eye irritant, Respiratory irritant	UV absorber	LC/MS/MS	X	X	O	O
Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate	Weak Aquatic toxicity	None	LC/MS/MS	O	X	X	X
Dodecylbenzenesulfonic acid	Aquatic toxicity	Surfactant	LC/MS/MS	X	X	X	X
Heptaethylene glycol p-tert-octylphenyl ether	None	Surfactant	LC/MS/MS	O	X	X	X
Hexamethylenetetramine	Weak irritant	Dye fixative	LC/MS/MS	O	X	X	X
Laurylsulfuric acid	Aquatic toxicity	Surfactant	LC/MS/MS	O	X	X	X
n-Octyl sulfate	None	Surfactant	LC/MS/MS	O	O	X	X
Triethylene glycol monobutyl ether	Eye damage	Plasticizer	LC/MS/MS	O	O	X	X
1,3-Propanediol, 2-ethyl-2-(hydroxymethyl)-	None	Alkyd resin precursor	py-GC/MS	O	X	X	X
2,6-Di-tert-butyl-4-hydroxy-4-methylcyclohexa-2,5-dien-1-one	Skin irritant, Eye irritant, Respiratory irritant, Weak oral toxicity	None	py-GC/MS	X	X	O	O
2-Hydroxyethyl methacrylate	Skin irritant, Eye irritant	Acrylic monomer	py-GC/MS	X	X	O	O
2-Propenoic acid, 1,7,7-trimethylbicyclo[2.2.1]hept-2-yl ester, exo- (isobornyl acrylate)	Strong aquatic toxicity	UV polymerization	py-GC/MS	X	X	O	X
Benzenamine, 2-methoxy- (o-anisidine)	Strong carcinogen, Mutagen	Dye precursor	py-GC/MS	X	O	X	O
Benzenamine, 3-methoxy- (m-anisidine)	Oral toxicity, Dermal toxicity, Inhalation toxicity, Strong Aquatic toxicity	Dye precursor	py-GC/MS	X	X	X	O
Benzenamine, 4-chloro-2,5-dimethoxy-	Oral toxicity, Strong Aquatic toxicity	None	py-GC/MS	X	X	X	O
Ethanol, 2-[2-(2-butoxyethoxy)ethoxy]-	Eye damage	Plasticizer	py-GC/MS	O	X	X	X
Isophorone diisocyanate	Skin irritant, Eye irritant, Inhalation toxicity, Aquatic toxicity	Used in polyurethane paints	py-GC/MS	X	X	O	O
Methenamine	Skin irritant	Dye, Antibiotic	py-GC/MS	O	X	X	X
n-Butyl methacrylate	Skin irritant, Eye irritant	Acrylic monomer	py-GC/MS	X	X	X	O
1,3-Pentanediol, 2,2,4-trimethyl-	None	Plasticizer	py-GC/MS, GC/MS	O	O	X	X
2-Propenoic acid, butyl ester	Skin irritant, Eye irritant, Respiratory irritant, Aquatic toxicity	Acrylic monomer	py-GC/MS, GC/MS	X	X	X	O
Octabenzone	Skin sensitizer, Aquatic toxicity	UV absorber	py-GC/MS, GC/MS	X	X	O	O
Propanoic acid, 2-methyl-, 3-hydroxy-2,2,4-trimethylpentyl ester	Aquatic toxicity	Coalescing agent	py-GC/MS, GC/MS	O	O	O	X

- MS analysis putatively identified 27 chemicals, five of which are highlighted in bold for their significant toxicity to humans and/or the environment.
- Most of the chemicals were detected using a single type of MS, which emphasizes the need to use multiple MS techniques to obtain a broader coverage of the chemicals present in the sample.

Conclusions

- Multiple complementary MS techniques were used to comprehensively identify potential organic pollutants in road marking paint samples.
- The presence of toxic chemicals in road marking paints suggests the need for toxicity evaluation of road marking paints.

Acknowledgements

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