

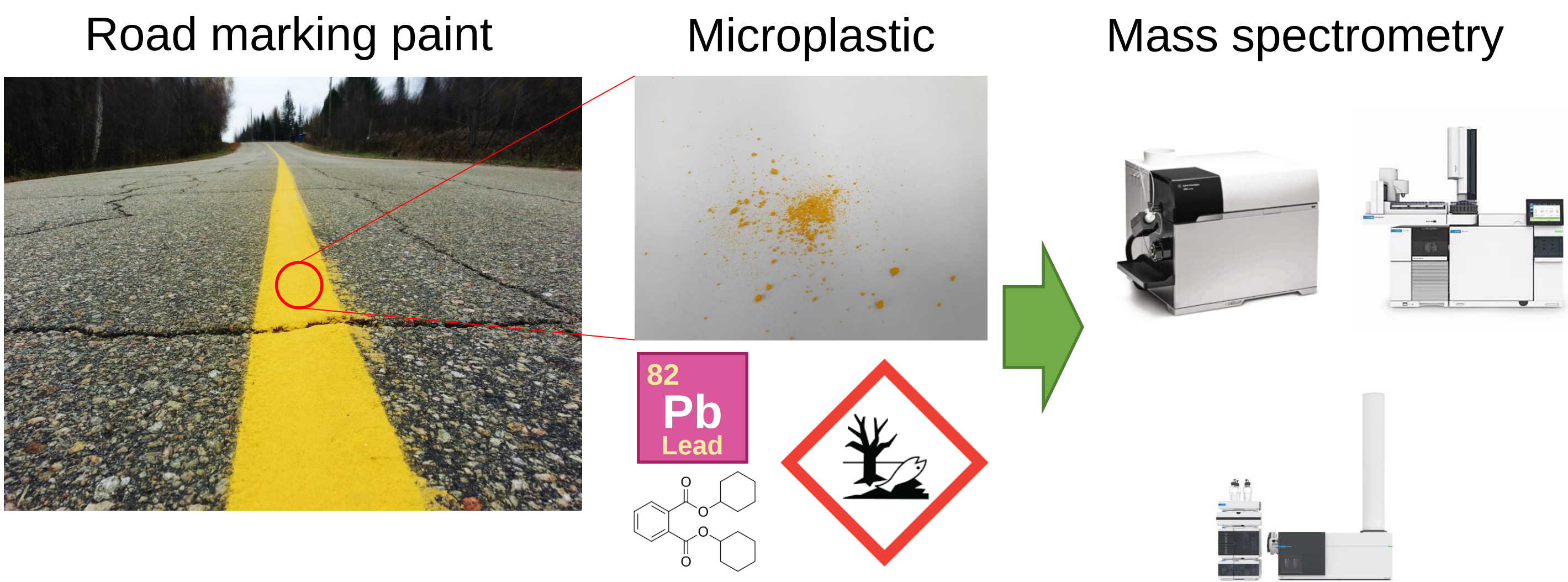
Integrated chemical analysis of road marking paint particles using complementary mass spectrometry techniques



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Introduction



- Road marking paints are a significant source of microplastics in soil environments.
- Hazard assessment of the chemical additives in road marking paints remains limited.
- This study employed multiple MS techniques to analyze the chemical profiles of four road marking paints.

Experimental

1. Sample preparation

2-Y

2-W

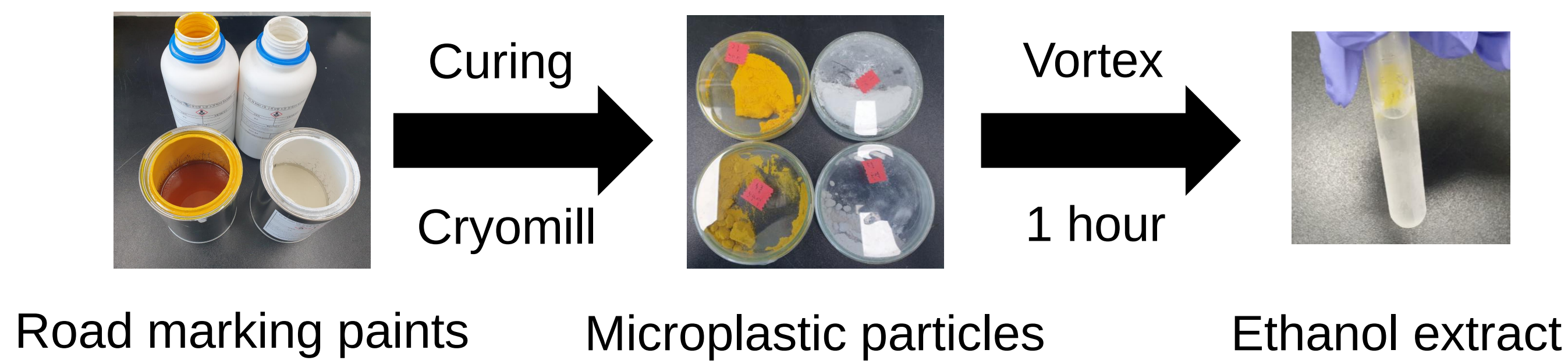
5-Y

5-W

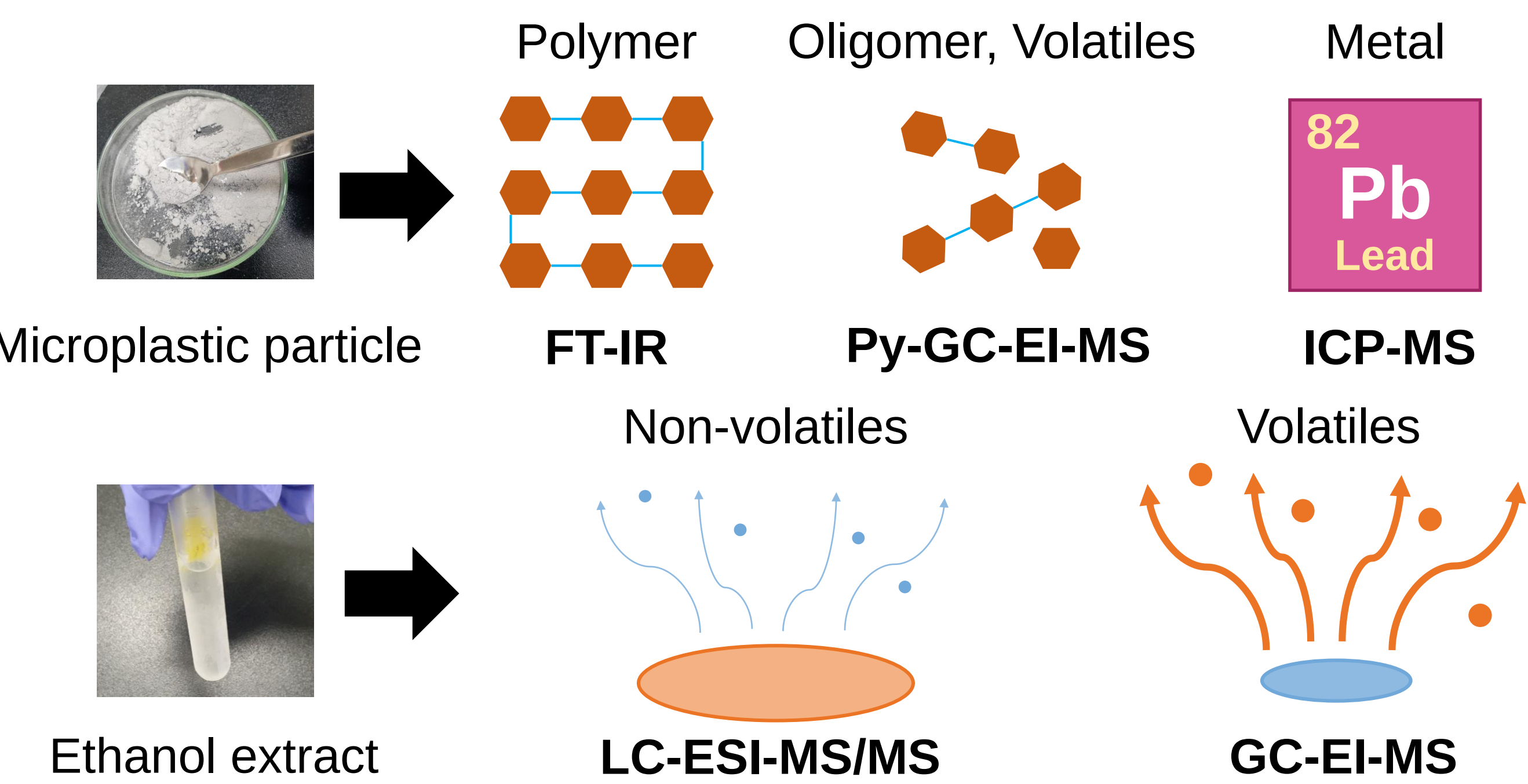
2-Y, 2-W: KS M 6080 type 2 paints, Waterborne (in aqueous solvent)

5-Y, 5-W: KS M 6080 type 5 paints, Coldplastic (chemically cured using curing agent)

2. Sample preparation



3. Sample Analysis



Results

1. FT-IR analysis of polymer

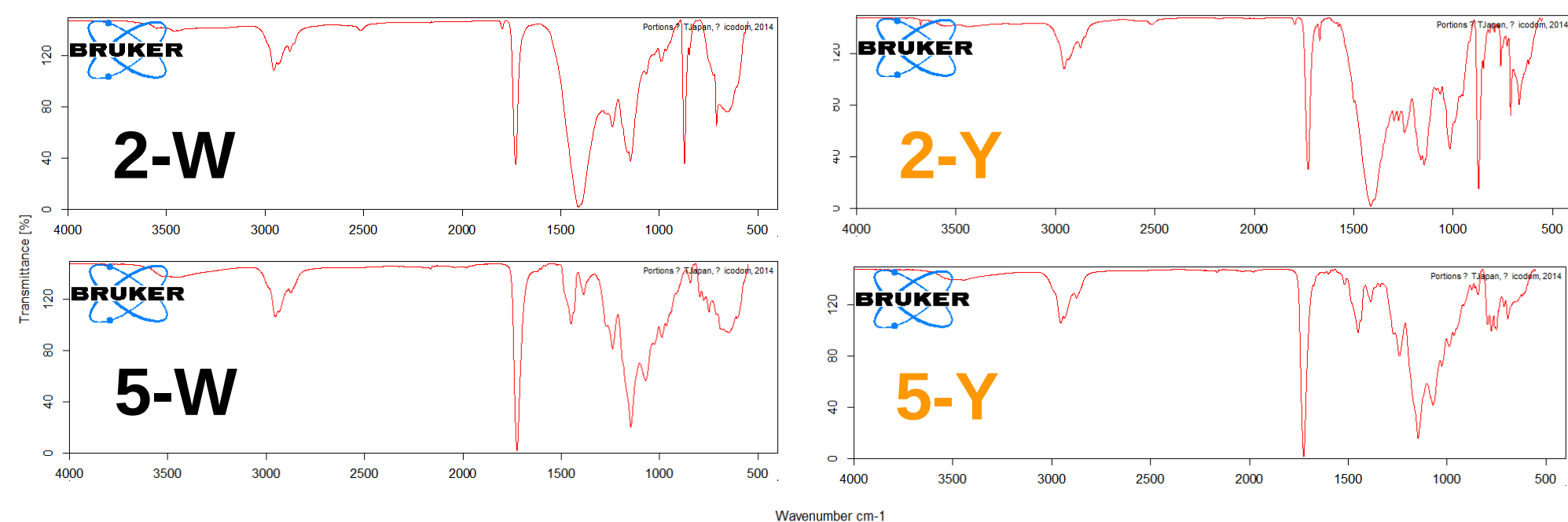


Figure 1. FT-IR spectra of the road marking paint samples

- FT-IR library search identified four paint samples as acrylic paints.
- Samples of 5-W and 5-Y were definitively identified as poly(methyl methacrylate) (PMMA) based on their library match.
- All samples exhibited characteristic peaks for PMMA at 3000 & 1700 cm⁻¹, indicating the presence of PMMA in samples of 2-W and 2-Y as well.

Results

2. ICP-MS analysis of metal

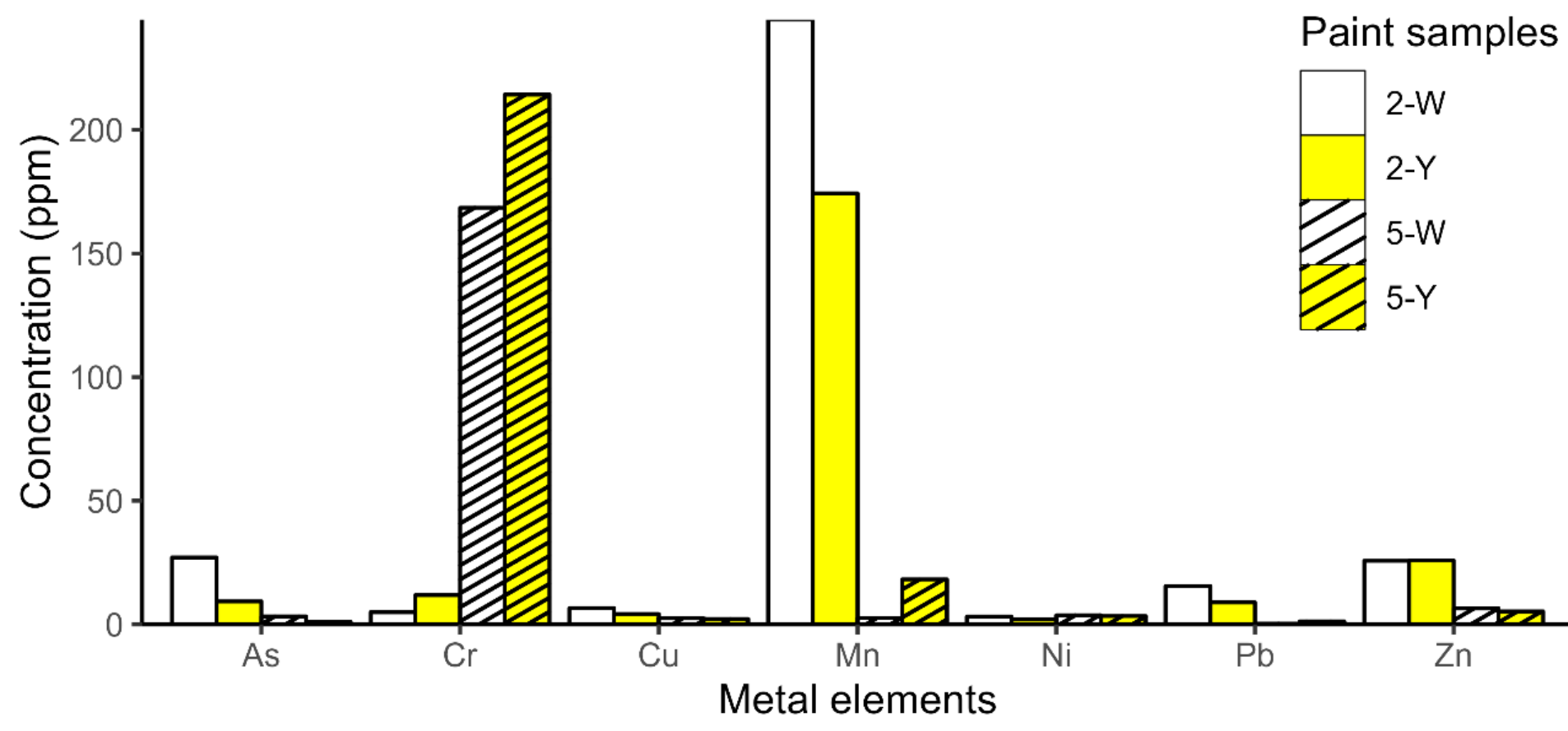


Figure 2. Metallic element contents of the four paint samples

- A large amount of chromium was detected in the 5-W and 5-Y paints. These paints may contain carcinogenic hexavalent chromium, necessitating further analysis.
- The arsenic content measured in the 2-W paint approached South Korea's soil contamination criteria of 25 ppm.
- The high concentrations of chromium detected in paints 5-W and 5-Y, and manganese in paints 2-W and 2-Y, likely originate from metallic pigments. However, the specific composition of pigments used in these road marking paints remains undisclosed by the manufacturer.

3. Organic additives identified by py-GC-MS, GC-MS, and LC-MS

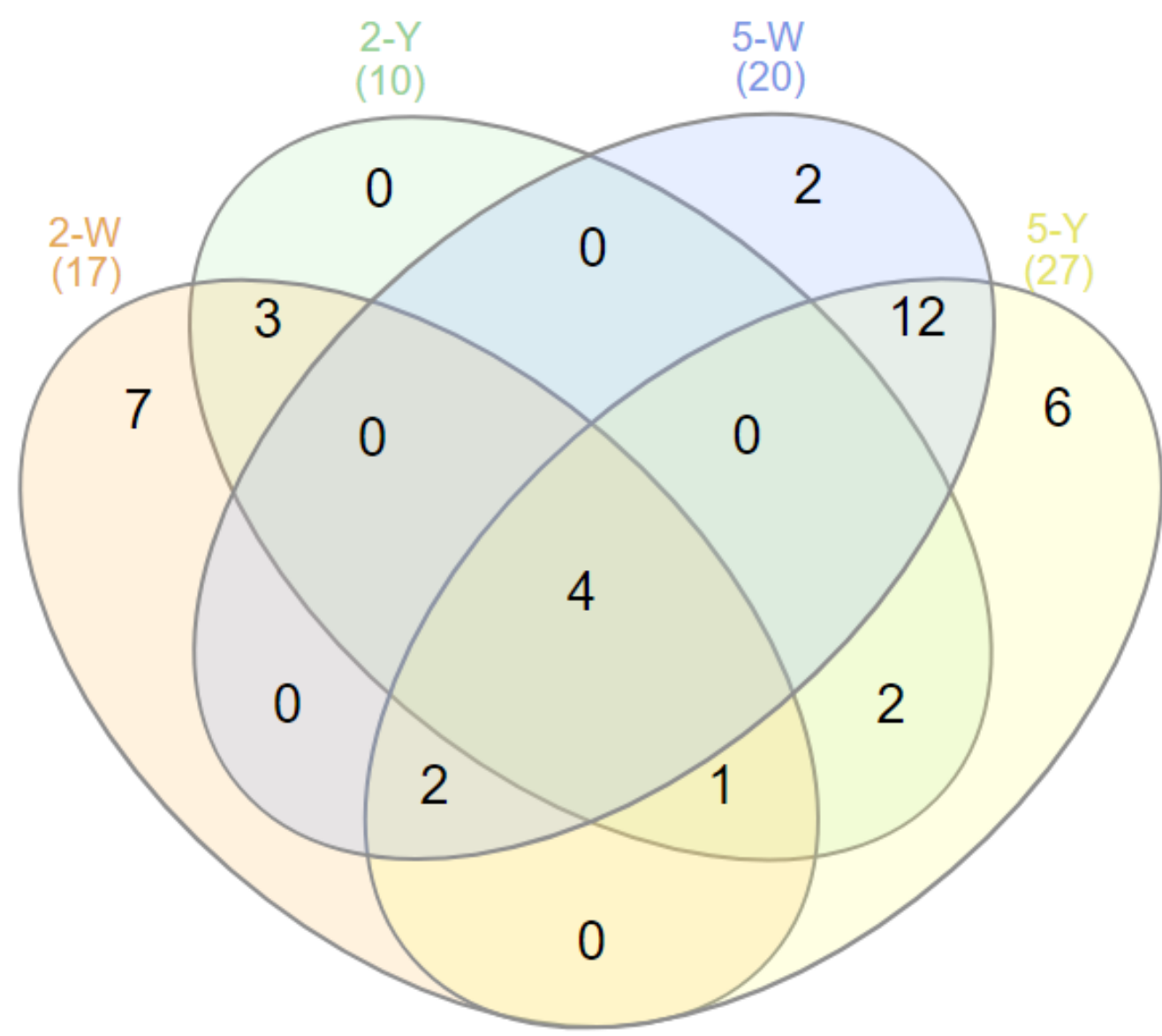


Figure 3. Venn diagram of organic additives. Numbers in parenthesis indicate the number of organic additive found in the corresponding sample.

- Following spectral library matching, only compounds identified within the PlasticMAP library (known plastic additive library) were selected for further analysis.
- A total of 39 unique organic plastic additives were identified across the four road marking paint samples.
- Significantly, a higher degree of additive overlap was observed between paints of the same type compared to paints of the same color.
- Four alkanes and fatty acid esters were common to all four road marking paint samples, suggesting their potential use as solvents..

4. Harmful organic additives in road marking paints

Table 1. Toxic organic additives found in four road marking paint samples. Color of cell denotes the instrument that detected the compound. **Peach**: py-GC-MS, **Yellow**: py-GC-MS and GC-MS, **Green**: GC-MS, **Cyan**: LC-MS

Hazard	Compounds			
Aquatic toxicity	Lauryl Alcohol	1-Dodecanethiol	Dodecyl methyl sulfide	Butyl Acrylate
	1-Tetradecanol	Butylated Hydroxytoluene	Methanethiol	Isobornyl acrylate
Health hazard	Isophorone diisocyanate (Resp. Toxicity)	O-Anisidine (Carcinogen)	Dicyclohexyl phthalate (Repr. Toxicity, EDC)	Tetramethrin (Potential Carcinogen)
	Trimethylolpropane (Potential Repr. Toxicity)	p-Cresol (Potential Carcinogen)	1-Dodecene (Resp. Toxicity)	2,4-Dihydroxybenzophenone (Potential Repr. Toxicity)

- The hazard classification of identified compounds was performed using the ECHA dossier GHS classification system.
- The application of py-GC-MS, GC-MS, and LC-MS analyses revealed distinct sets of compounds in the samples, with some overlap observed between py-GC-MS and GC-MS data.
- Several high-risk compounds were identified in the road marking paint samples, including isophorone diisocyanate, o-anisidine, dicyclohexyl phthalate, and 1-dodecene.
- The high number of compounds exhibiting aquatic toxicity raises concerns about their potential impact on the soil environment as well. The current GHS classification system does not evaluate this aspect.

Conclusions

- The study identified various toxic chemicals in road marking paints using multiple MS techniques.
- The presence of hazardous organic additives necessitates further toxicity evaluation of road marking paints.

Acknowledgements

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