HOW TO DETERMINE OLEFINS IN PYROLYSIS/HTL OILS FROM WASTE PLASTICS AND TIRES USING GC×GC-FID?

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INTRODUCTION

Olefins create the major hydrocarbon group in pyrolysis oils (PO) from waste plastics and tires, accounting for over 70 wt%. As olefins are responsible for low thermo-chemical stability and difficulties during the valorization of those oils, the reliable and accurate determination of olefins is thus essential.

The identification of olefins, even with high-resolution techniques such as GC×GC, remains challenging as they coelute with other hydrocarbon groups, primarily naphthenes. Specific detectors, such as PI-TOF-MS or VUV, are required for the selective monitoring of olefins. Currently, the only method for the selective determination of olefins in plastic pyrolysis oils is GC-VUV, which has recently been standardized as ASTM D8519. However, PI-TOF-MS and VUV are not affordable instruments for many research teams working on plastic recycling. ***We developed a simple solution for you!***

METHODOLOGY

The olefins separation procedure over Ag-SiO_2 was optimized using several mixtures of model compounds. The final separation scheme is as follows:

- 3 mL SPE cartridge
- 1.45±0.03 g (±2.5 mL) of freshly activated Ag-SiO_2 (p.s. 0.040–0.063 mm)
- Sorbent densified and fixed by frit
- 15 µL (approx. 12-14 mg) of sample
- Eluted by Dichloromethane (DCM) dosed in 0.6 mL portions
- The first 1.8 mL effluent was collected into a 2 mL GC vial
- Sample elution solely supported by gravity

→ GC×GC-FID analysis of the sample before and after separation

Loss in peak area in the respective regions before and after separation corresponds to olefin content.
Peak area normalization is required, using an externally added or native internal standard.

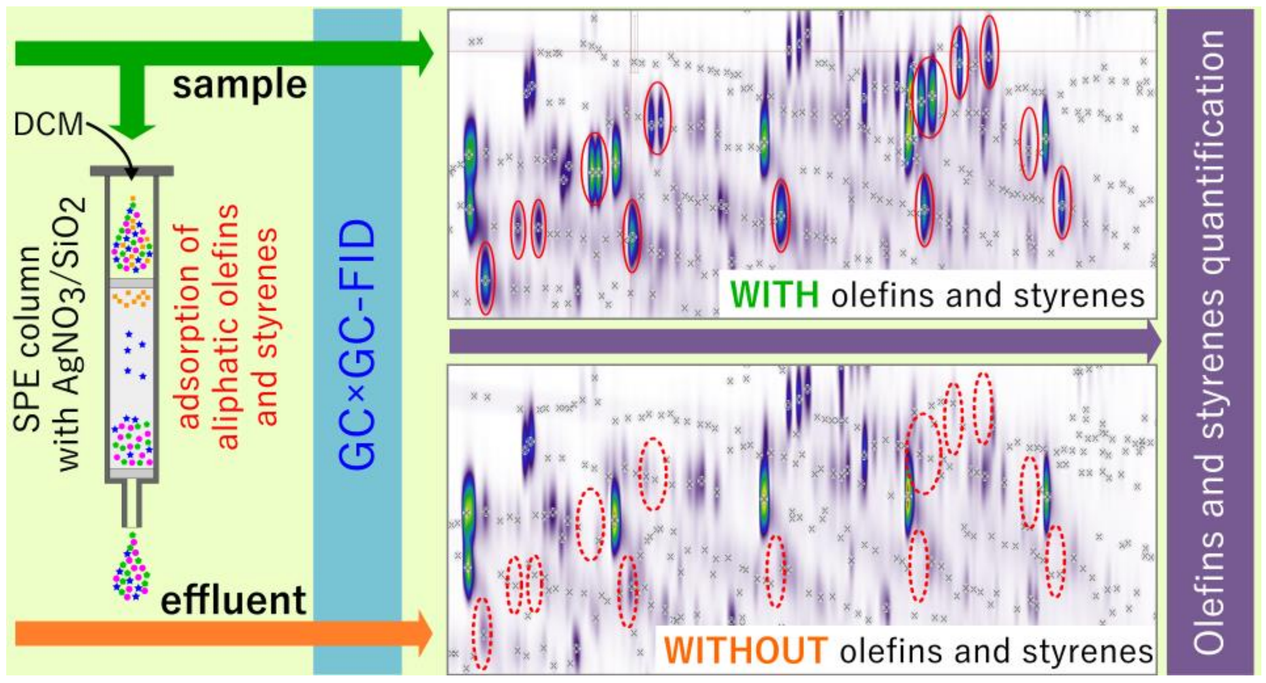

Table 1: Results for JET-A1 spiked by olefinic model compound mixture (validation)

Aliphatic olefins content			
Prepared (wt%)	Determined (wt%)	RSD (%)	Difference (rel.%)
34.90	35.88	0.4	2.8
17.54	17.55	1.7	0.1
8.41	8.35	3.3	-0.6
4.37	4.29	9.0	-1.7
2.32	2.17	21.1	-6.5
0.94	0.49	31.6	-47.5
0.43	-0.67	-	-
0.00	-0.03	-	-

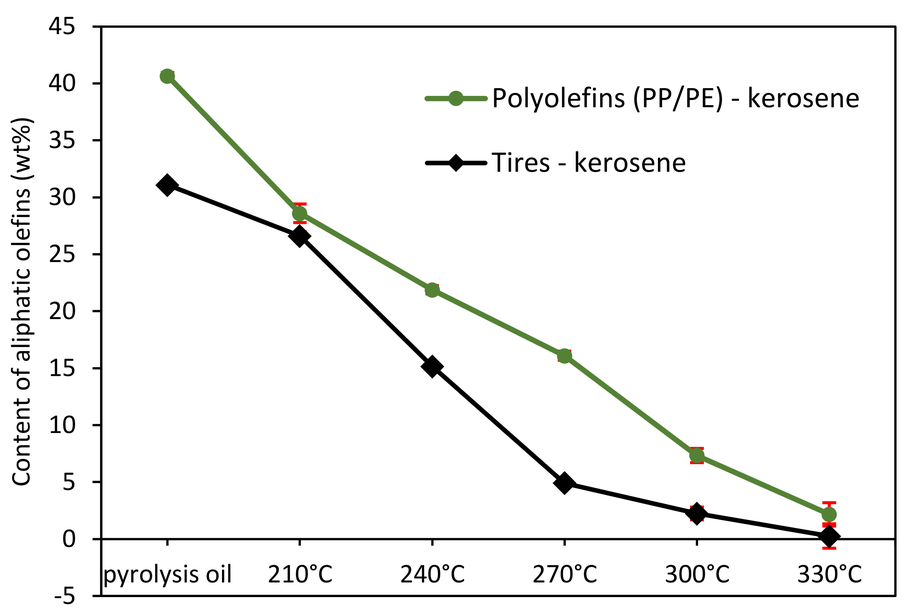

Figure 1: Olefin content in PO before and after hydrotreatment

Table 2: Results for pyrolysis oils from sorted waste polyolefins, mixed waste plastics rich in contaminants (MWP), and tires.

Olefins in	PP/PE (wt%)	RSD (%)	PE 2 (wt%)	RSD (%)	MWP 1 (wt%)	RSD (%)	MWP 2 (wt%)	RSD (%)	Tires 1 (wt%)	RSD (%)	Tires 2 (wt%)	RSD (%)
n-alkanes	4.79	0.96	10.09	1.02	12.25	1.89	1.55	7.33	0.14	9.1	0.17	11.7
i-alkanes	14.38	0.16	37.91	0.87	21.37	1.27	5.21	1.35	0.70	23.6	0.34	4.2
monocycloalkanes	8.44	0.69	14.35	0.47	18.20	0.45	34.35	0.12	2.28	3.7	1.99	0.9
dicykloakanes	1.35	2.82	6.29	0.46	6.34	0.60	11.52	0.45	13.52	0.9	5.25	0.5
tricycloalkanes	0.02	13.55	0.27	0.84	0.28	0.94	0.48	3.67	11.13	0.1	1.61	0.6
Total aliphatic olefins	28.99	0.48	68.91	0.76	58.44	0.95	53.12	0.42	27.76	1.4	9.36	0.5
styrenes	2.14	3.43	3.19	4.73	1.81	2.98	2.37	4.05	4.37	3.2	2.86	6.9

CONCLUSIONS AND HIGHLIGHTS

- Method **application range** – olefins concentration **> 5 wt%**
- The **cheap and straightforward solution → higher accuracy and reliability in olefin determination**
- The method is based on the **adsorption of olefins over $AgNO_3/SiO_2$**, followed by the **GC×GC-FID analysis**
- **No MS detector** and MS spektra interpretation **required**
- Only **50 µL of sample and 15 min** of sample preparation needed

For more details see our publication

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