Gas Chromatography Coupled to Atmospheric Pressure Chemical Ionization FT-ICR Mass Spectrometry for Improvement of Data Reliability

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Table S-1: Sample acquisition and preparation

engine	four stroke single-cylinder direct-injected ship diesel test engine
used fuels	heavy fuel oil (HFO 180) and distillate fuel (DF) according to EN 590
sample acquisition	engine exhaust gas was collected for four hours on quartz fiber filter discs after cooling the exhaust gas to near room temperature by appropriate dilution with compressed air
exhaust gas dilution ratios	1:10 for diesel fuel and 1:40 for heavy fuel oil
sample preparation particulate matter	the filters were extracted twice with 25 ml methanol/dichloromethane (50/50, v/v) for 15 min using an ultrasonic bath. Both extractions were combined and filtered via a 0.2 µm PTFE-membrane filter. An aliquot of 5 mL was concentrated to about 0.1 mL by applying a stream of pure nitrogen at room temperature
sample preparation fuel	1:100 dilution in a mixture of methanol/dichloromethane (50/50, v/v) and directly analyzed without further treatments

Table S-2: GC parameters

GC Type	CP 3800 (Agilent, former Varian Technologies, Palo Alto, CA, USA)
injector	1079 programmable temperature vaporizer injector equipped with a ChromatoProbe device
column	HT5 column (25 m length x 0.53 mm i.d. x 0.15 µm film thickness, SGE Analytical Science, Australia)
injection	splitless
injection volume	2 µL
injection program	60°C (1 min) → 300°C with 50°C/min
oven program	40°C(6 min)→ 320°C with 10°C/min
flow rate	constant at 10 mL/min of 99.999% Helium
temperature transfer line	320°C

Table S-3: APCI source and FT-ICR MS parameters

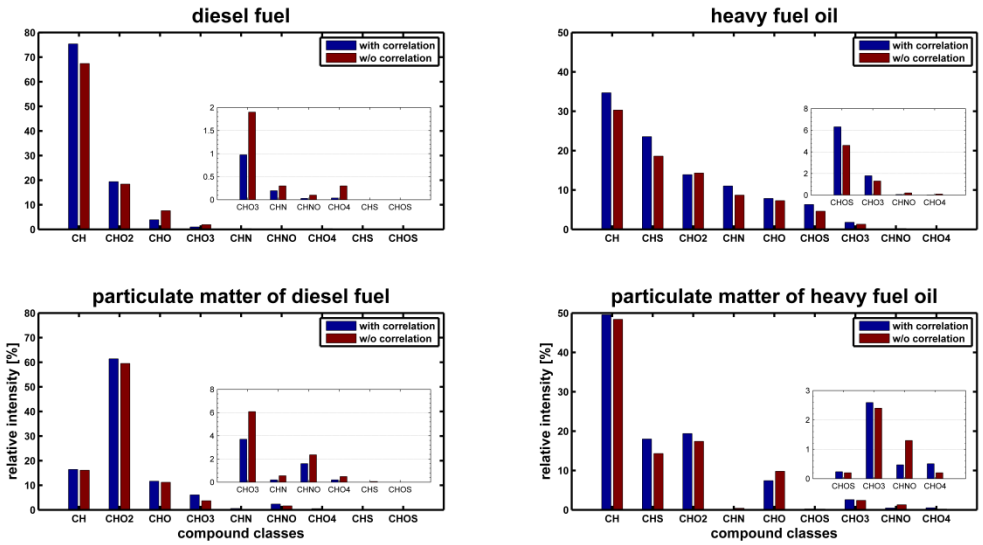
source	atmospheric pressure chemical ionization source with a specialized gas phase inlet[16]
mass spectrometer	Apex Qe Series II FT-ICR MS system (Bruker Daltonics, Billerica, MA, USA / Bruker Daltonics GmbH, Bremen, Germany)
magnet	7 T magnet (Bruker Biospin, France)
operating mode	positive mode
needle current	3 µA
source temperature	320 °C
sheath gas	nitrogen with a flow rate of 2 L/min
auxiliary gas	nitrogen with a flow rate of 0.6 L/min
dry gas	nitrogen with a flow rate of 2 L/min
nebulizer gas	nitrogen with a pressure of 3×10^5 Pa
acquisition rate	approximately 0.6 Hz
resolution at m/z 300	200 000
mass range	100 – 700 Da
acquisition software	Bruker Compass Data Analysis 4.0 SP 5 software package
transient operations	zero-filled, square sine-bell apodization and fast Fourier transformation into frequency domain applied
mass-calibration	precalibration with fatty acid methyl ester mix (C10 - C24; Supelco, Bellefonte, PA, USA) and internal calibration with an averaged mass spectrum of the chromatogram, using well known PAH signals of the samples and column bleed covering a m/z-range of 128 to 540
standard deviation of linear mass calibration	< 0.3 ppm
used Signal-to-noise ratio for export to MATLAB	≥ 9

Table S-4: Compound class distribution of fuels and particulate matter with applied KI correlation based on intensity weights

compound classes	diesel fuel	heavy fuel oil	particulate matter of diesel fuel	particulate matter of heavy fuel oil
CH	75.4%	34.8%	15.5%	48.8%
CHO	3.9%	7.8%	11.6%	11.5%
CHO2	19.4%	13.9%	61.4%	17.0%
CHO3	1.0%	1.8%	6.1%	2.3%
CHO4	0.0%	0.0%	0.5%	0.5%
CHN	0.2%	11.0%	0.6%	0.8%
CHNO	0.0%	0.1%	2.4%	1.4%
CHS	0.0%	23.6%	0.1%	15.6%
CHSO	0.0%	6.3%	0.0%	0.2%
others	1.1%	0.7%	2.8%	2.0%

Table S-5: Polycyclic aromatic hydrocarbons used for calibration of retention index with corresponding Kováts Indices from NIST08 database

number	**substance**	**elemental composition**	**protonated *m/z* [Da]**	**Kováts Index [IU]**
1	Naphthalene	$C_{10}H_8$	129.06988	1187.3
2	Acenaphthylene	$C_{12}H_8$	153.06988	1460.8
3	Acenaphthene	$C_{12}H_{10}$	155.08553	1479.9
4	Fluorene	$C_{13}H_{10}$	167.08553	1582.9
5	Phenanthrene	$C_{14}H_{10}$	179.08553	1775.0
6	Pyrene	$C_{16}H_{10}$	203.08553	2111.7
7	Chrysene	$C_{18}H_{12}$	229.10118	2458.5
8	Benzo[a]pyrene	$C_{20}H_{12}$	253.10118	2765.1
9	Dibenz(gh)anthracene	$C_{22}H_{14}$	279.11683	n.a.
10	Benzo[ghi]perylene	$C_{22}H_{12}$	277.10118	3151.6
11	Coronene	$C_{24}H_{12}$	301.10118	n.a.



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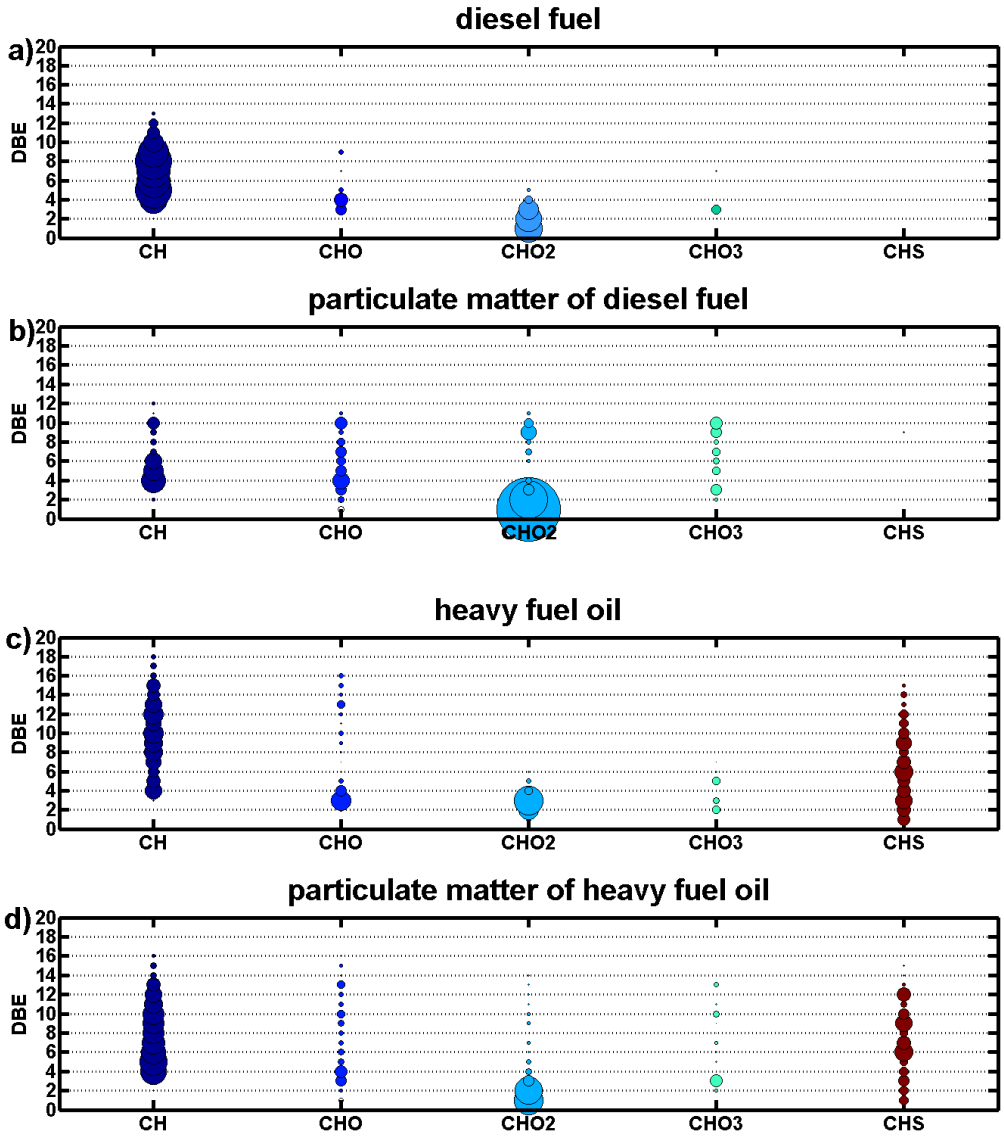

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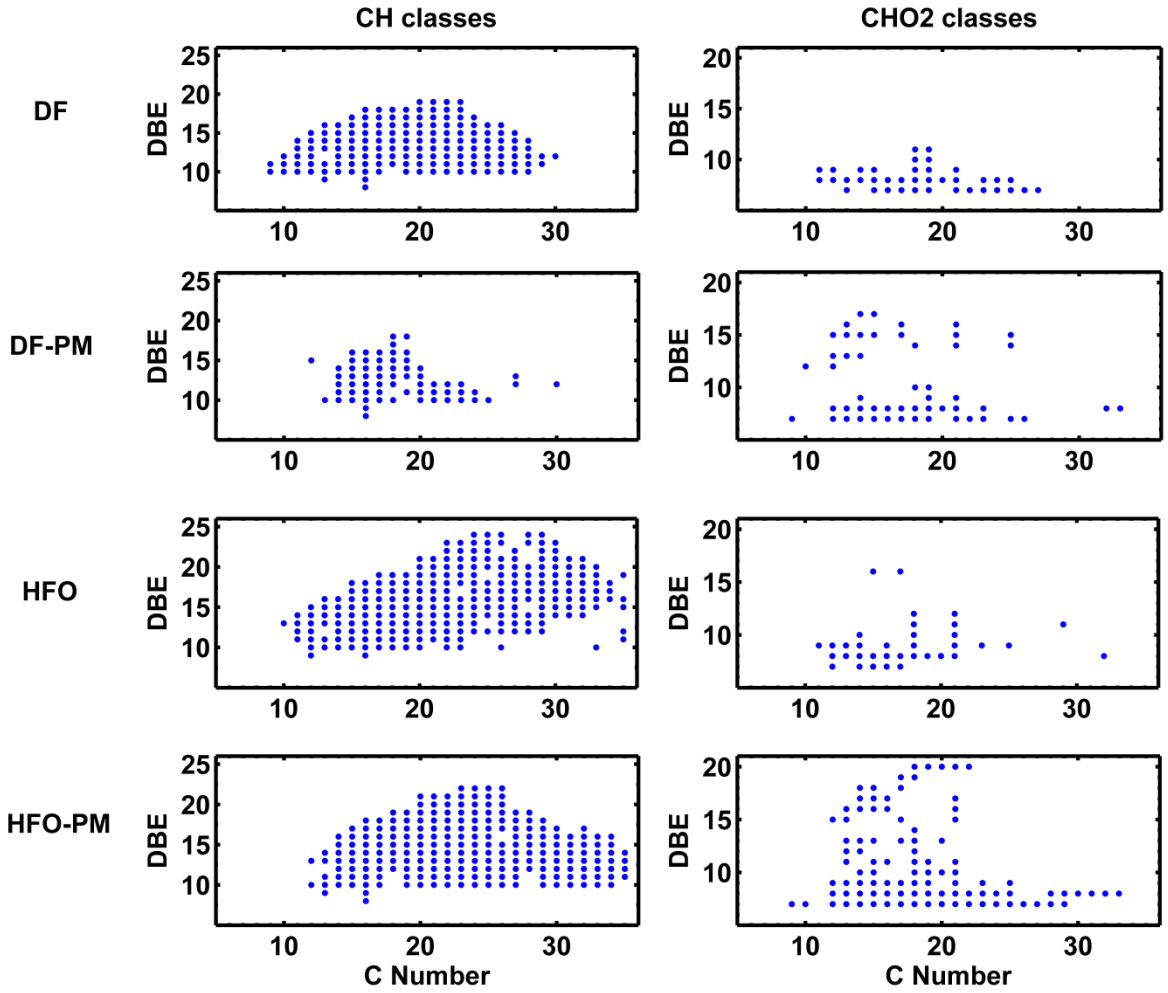

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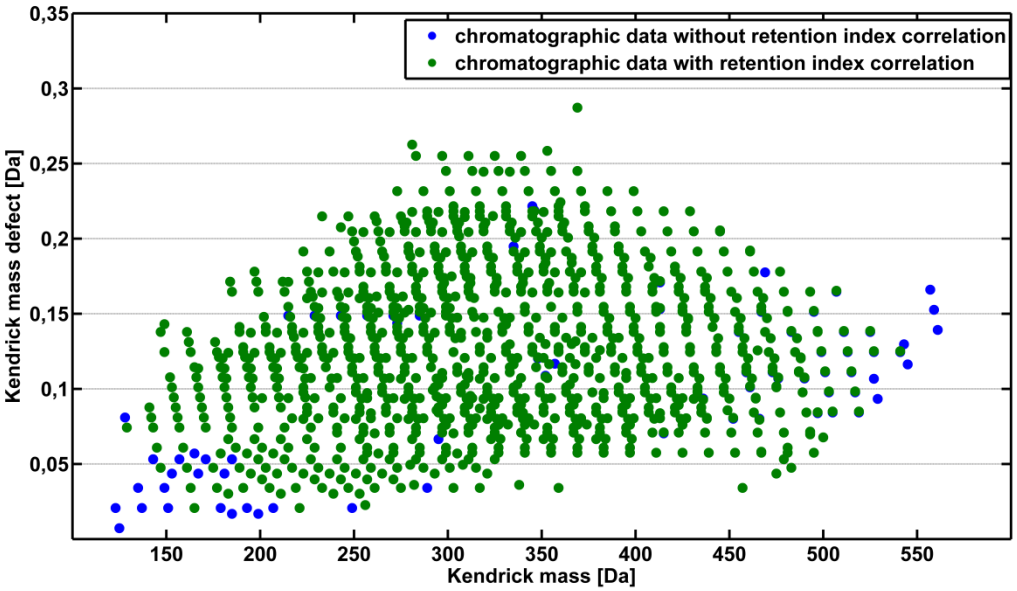

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