Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary information

Quantitative Multiplexed Elemental (C, H, N and S) Detection in Complex Mixtures using Gas Chromatography

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Experimental Procedures

All organic compounds injected, obtained pure from Sigma Aldrich, were diluted in hexane and dichloromethane. Combustion oven was obtained from Carbolite Hero (MFT 12/25/250). The valve employed was a two-position six-way stainless-steel valve with a 0.25 mm bore designed for operation at temperatures up to 350°C. All analyses were performed with a GC–MSD instrument (6890N GC coupled to a 5973Network quadrupole mass spectrometer, Agilent Technologies) equipped with an electron ionization source. Detailed conditions are given in Table S-1 and S-2.

Table S1. Experimental GC-combustion-MS conditions for the quantitative analysis of S- and N-containing standards.

Column flow	1.5 mLmin^{-1}
Temperature gradient	45˚C (3 min), 15˚Cmin^{-1} to 120˚C, 10˚Cmin^{-1} to 190˚C, 15˚Cmin^{-1} to 250˚C (1 min)
Column	Rxi-1ms (30 m x 0.32 mm x 1 µm) for S- compounds
	BD-EN14103, 30 m x 0.32 mm x 0.25 µm for N-compounds
Injection mode	Splitless
Inlet temperature	250˚C
Injection volume	1 µL
Combustion reactor	925°C, 0.4 mLmin^{-1} O_2/He for S compounds
	1150°C, 0.4 mLmin^{-1} O_2/He for N compounds
Acquisition mode	*SIM*: m/z 18, 30, 44, 48, 64

Table S2. Experimental GC-combustion-MS conditions for characterization of petroleum derivatives samples.

Column flow	1.5 mLmin^{-1}
Temperature gradient	45˚C (3 min), 8˚Cmin^{-1} to 250˚C (20 min)
Column	Rxi-1ms (30 m x 0.32 mm x 1 µm) for sulfur quantification and H/C ratio
	BD-EN14103, 30 m x 0.32 mm x 0.25 µm for nitrogen quantification
Injection mode	Splitless
Inlet temperature	250˚C
Injection volume	1 µL
Combustion reactor	925°C, 0.4 mLmin^{-1} O_2/He for S compounds
	1150°C, 0.4 mLmin^{-1} O_2/He for N compounds
Acquisition mode	*SIM*: m/z 18, 30, 44, 48, 64

Results and Discussion

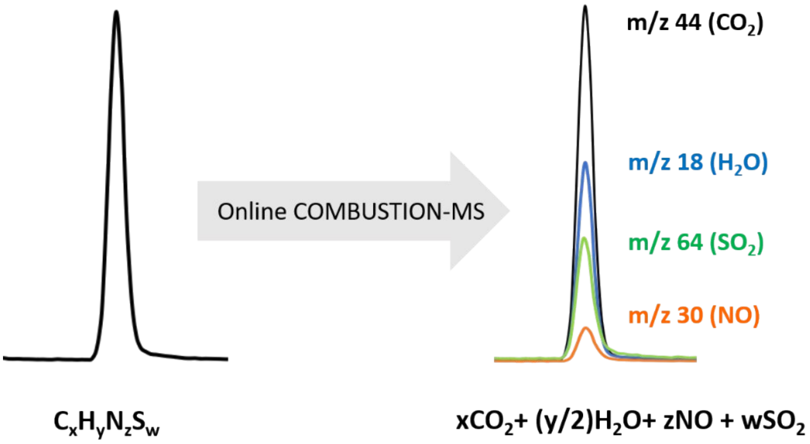


Figure S1. Schematic of the process and reactions occurring in the combustion mode to every organic species eluting from the column (left panel). Multiplexed element specific detection and quantification is carried out through the volatile species formed as indicated (right panel).

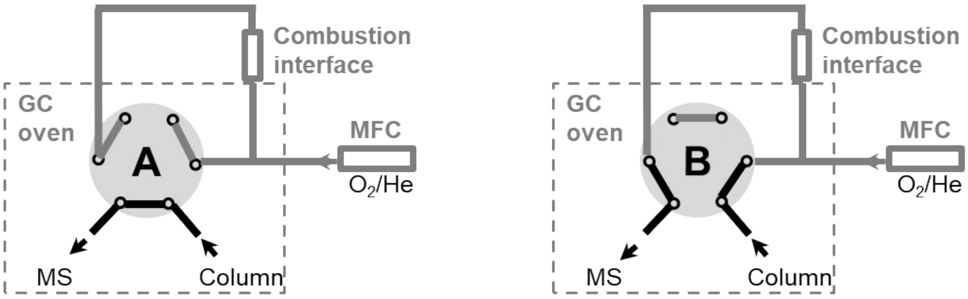


Figure S2. Diagram of the GC-combustion-MS setup with the two valve configurations: A) GC-MS conventional mode (structural elucidation) and B) GC-combustion-MS mode: C-, H-, N-, S-selective generic quantification.

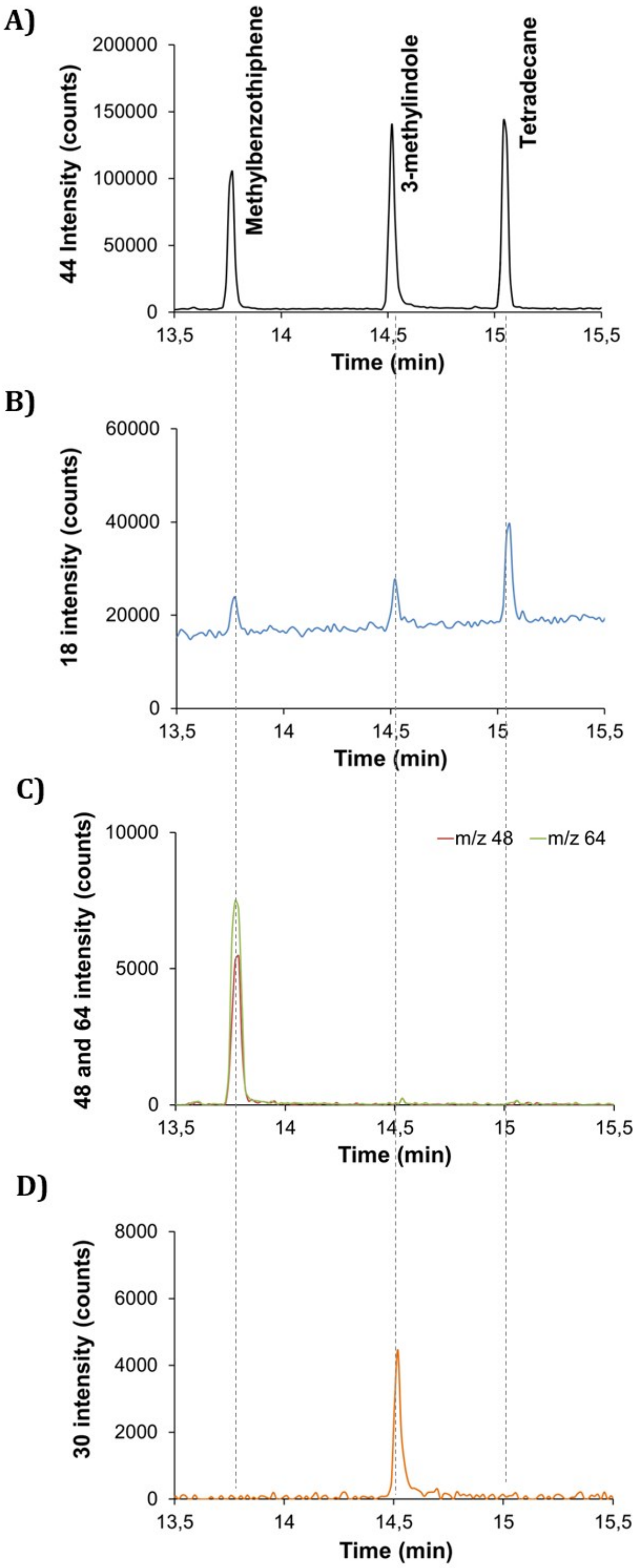
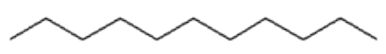


Figure S3. GC-combustion-MS chromatogram for A) m/z 44 (CO_2), B) m/z 18 (H_2O), C) m/z 48 y 64 (SO and SO_2) and D) m/z 30 (NO) obtained at 925°C and 0.4 mLmin^{-1} O_2/He for the mixture of 3-Methylbenzothiophene, 3-Methylindole and tetradecane. Signal to noise ratio is low because the chromatogram was acquired in scan mode (12-300 u) in order to monitor the species combustion and the formation of the corresponding volatile species.

Undecane

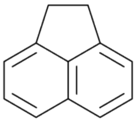


Tetradecane

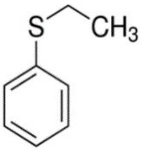
Heptadecane

Pentadecane

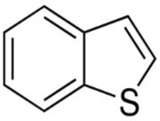
Acenaphthene



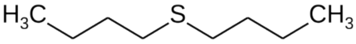
Ethyl phenyl sulfide



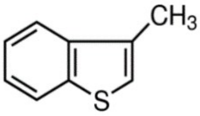
Benzothiophene



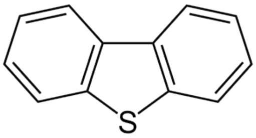
Dibutyl sulfide



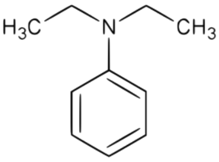
3-Methylbenzothiophene



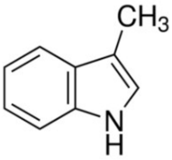
Dibenzothiophene



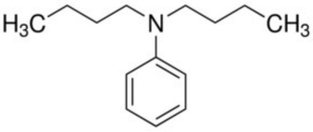
N,N-Diethylaniline



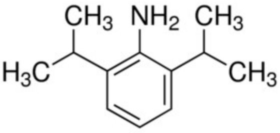
3-Methylindole



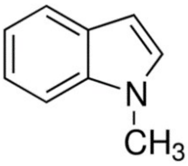
N,N-Dibutylaniline



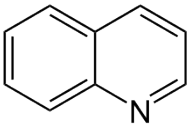
2,6-Diisopropylaniline



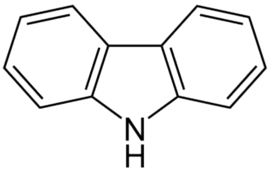
1-Methylindole



Quinoleine



Carbazole



Indole

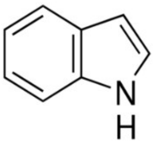


Figure S4. Structures of S-, N-containing and organic compounds present in the model mixtures.

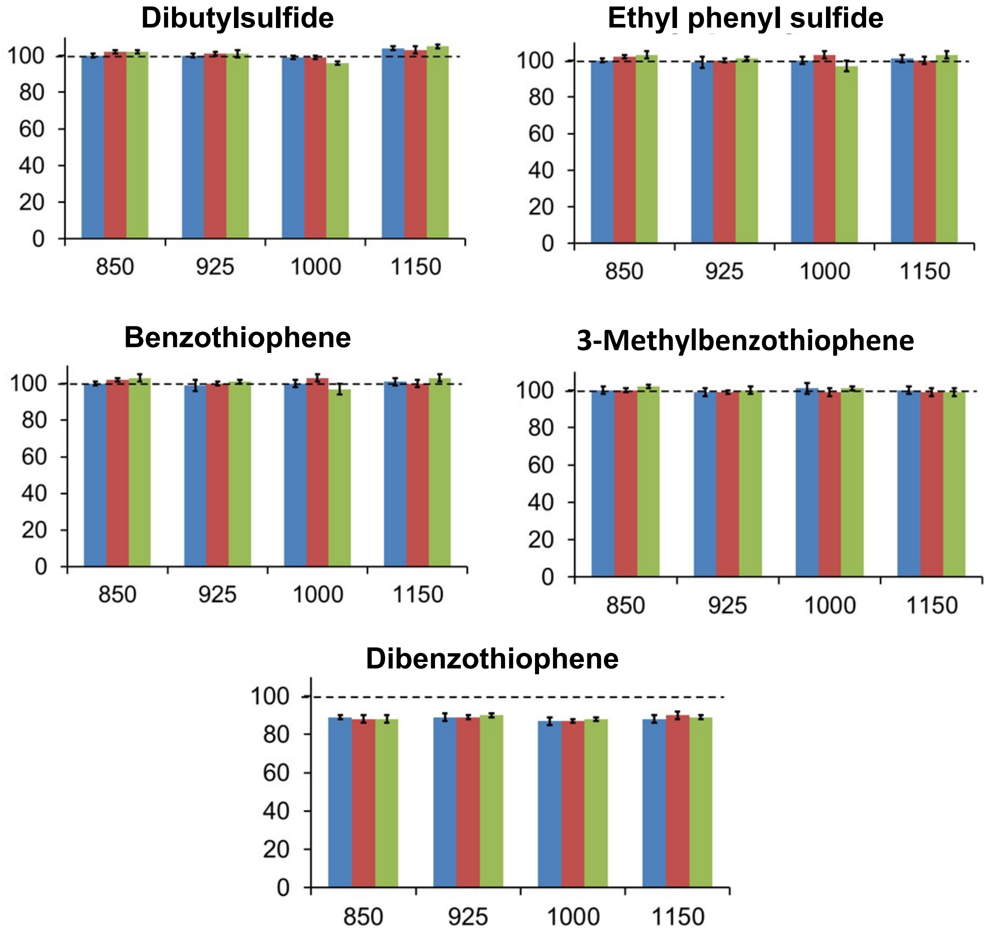


Figure S5. CO_2 recoveries (m/z 44) for S-containing compounds at different temperatures (850-1150°C) and 0.1, 0.2 and 0.4 mLmin^{-1} O_2/He (blue, red and green bars, respectively) using tetradecane as internal standard. Error bars indicate 1 SD (n=3).

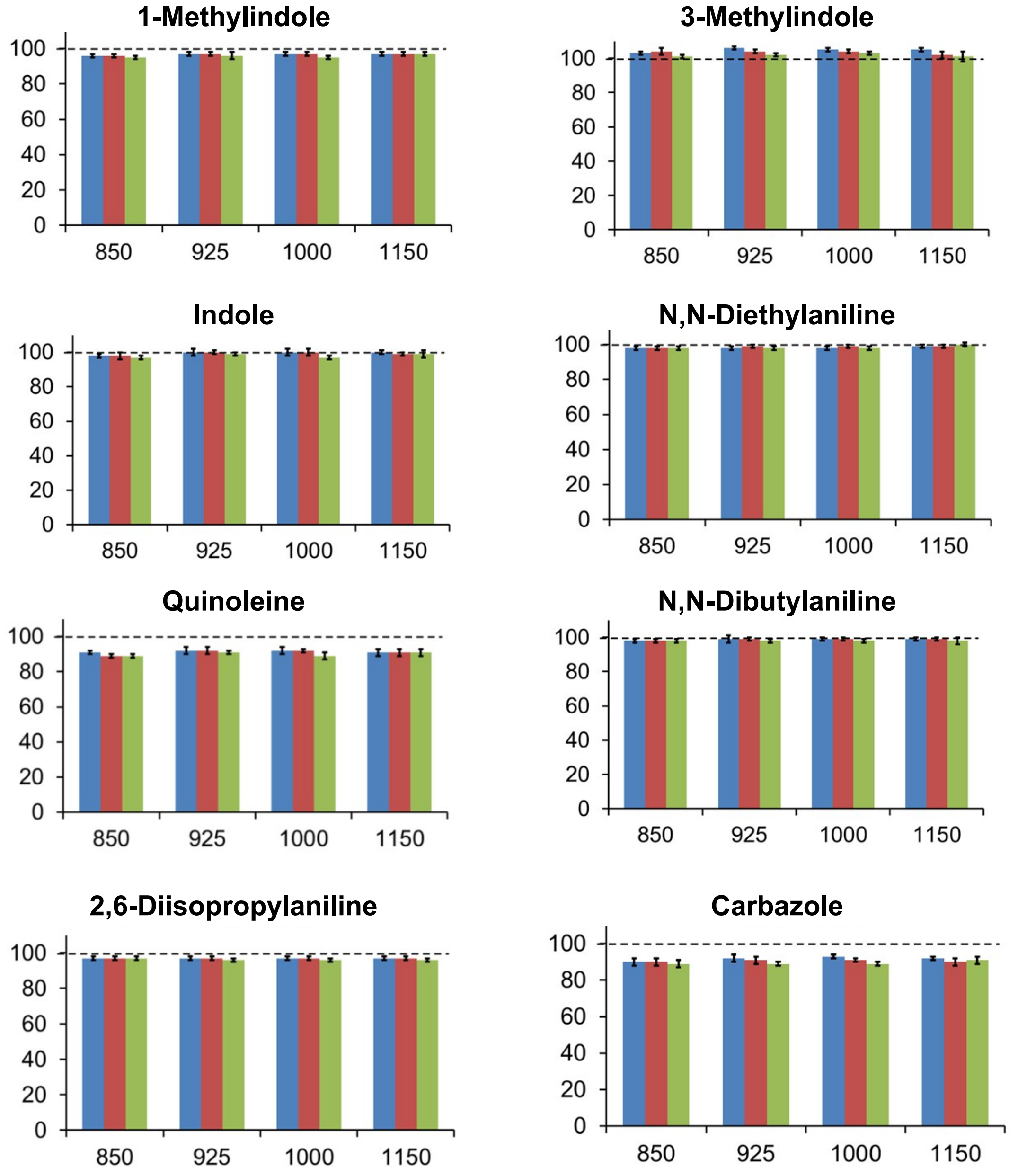


Figure S6. CO_2 recoveries (m/z 44) for N-containing compounds at different temperatures (850-1150°C) and 0.1, 0.2 and 0.4 mLmin^{-1} O_2/He (blue, red and green bars, respectively) using pentadecane as internal standard. Error bars indicate 1 SD (n=3).

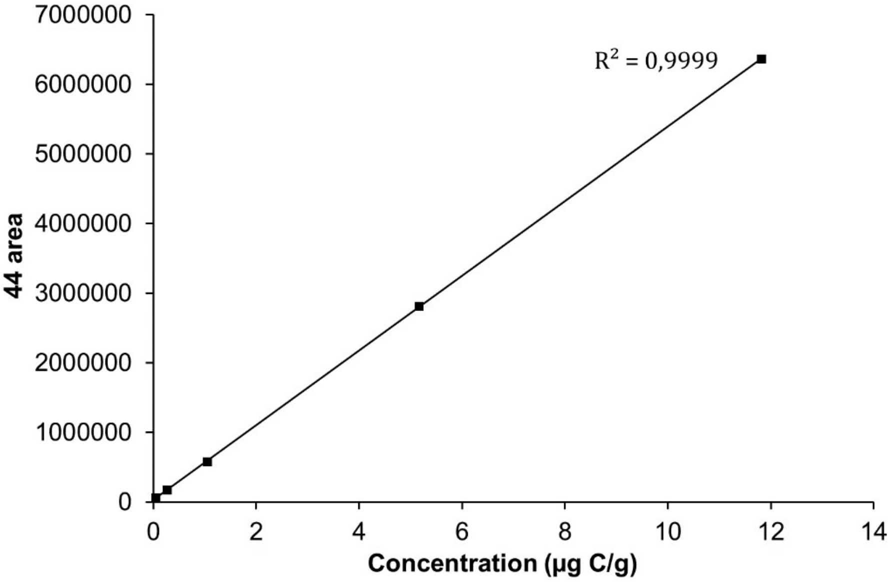


Figure S7. Linearity for acenaphthene from 0.050 to 12 µg C g^{-1} using 925°C and 0.4 $mLmin^{-1}$ O_2/He.

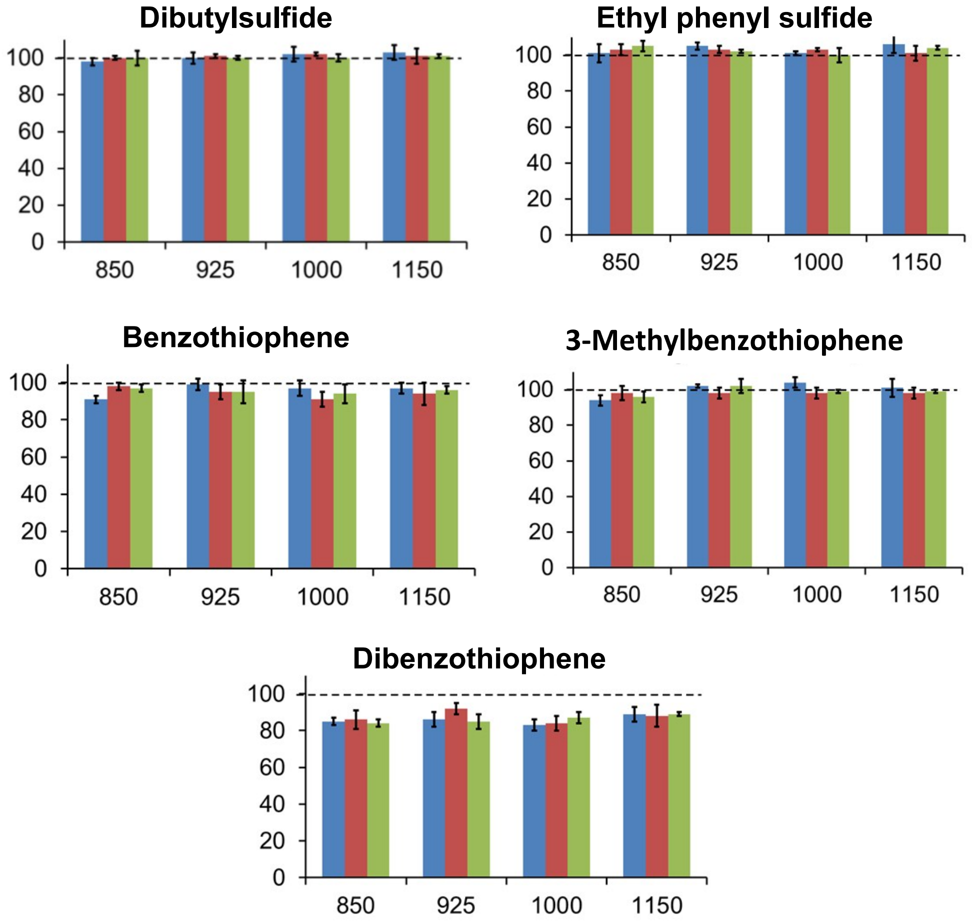


Figure S8. H_2O recoveries (m/z 18) for S-containing compounds at different temperatures (850-1150°C) and 0.1, 0.2 and 0.4 mLmin^{-1} O_2/He (blue, red and green bars, respectively) using tetradecane as internal standard. Error bars indicate 1 SD (n=3).

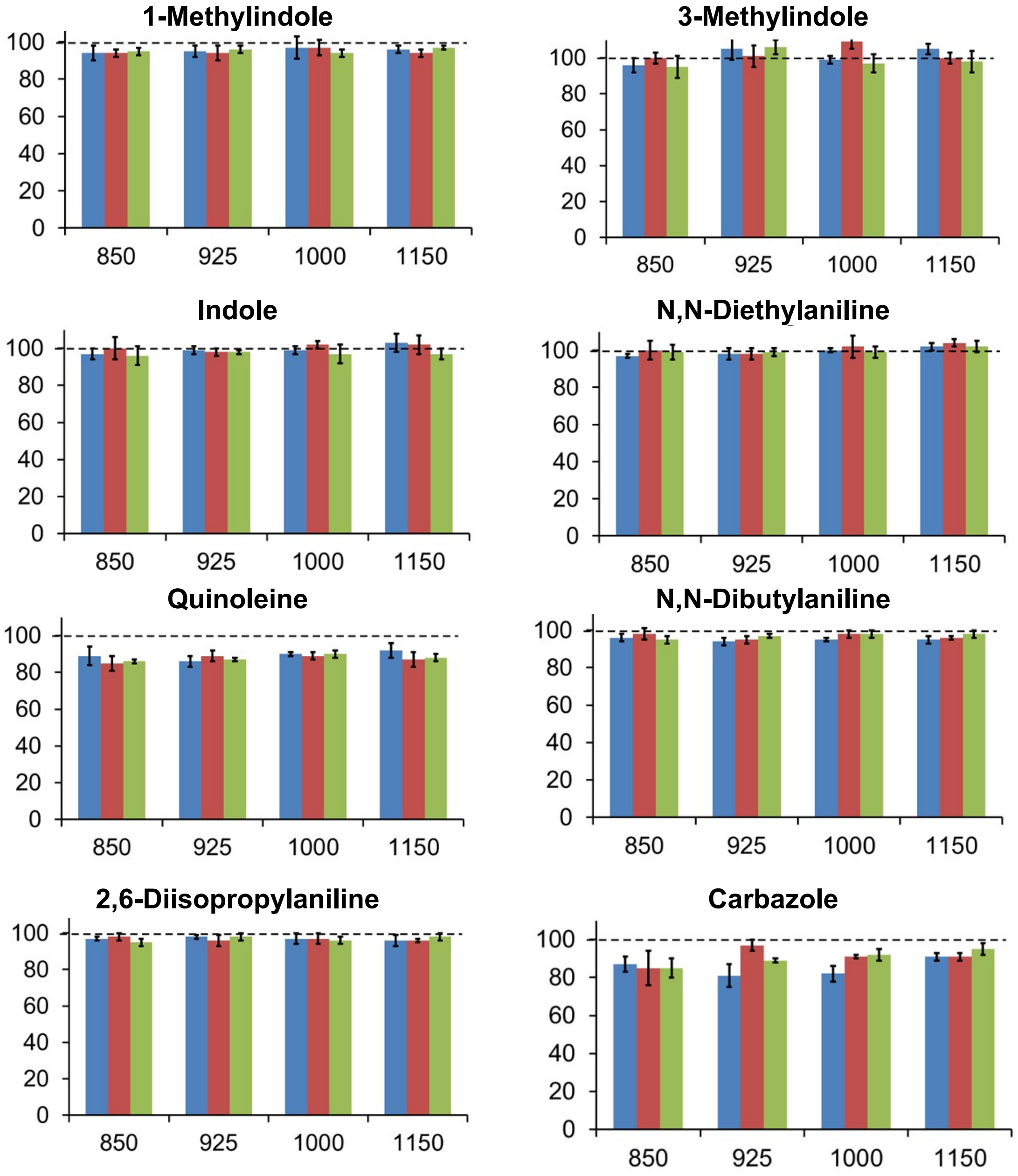


Figure S9. H_2O recoveries (m/z 18) for N-containing compounds at different temperatures (850-1150°C) and 0.1, 0.2 and 0.4 $mLmin^{-1}$ O_2/He (blue, red and green bars, respectively) using pentadecane as internal standard. Error bars indicate 1 SD (n=3).

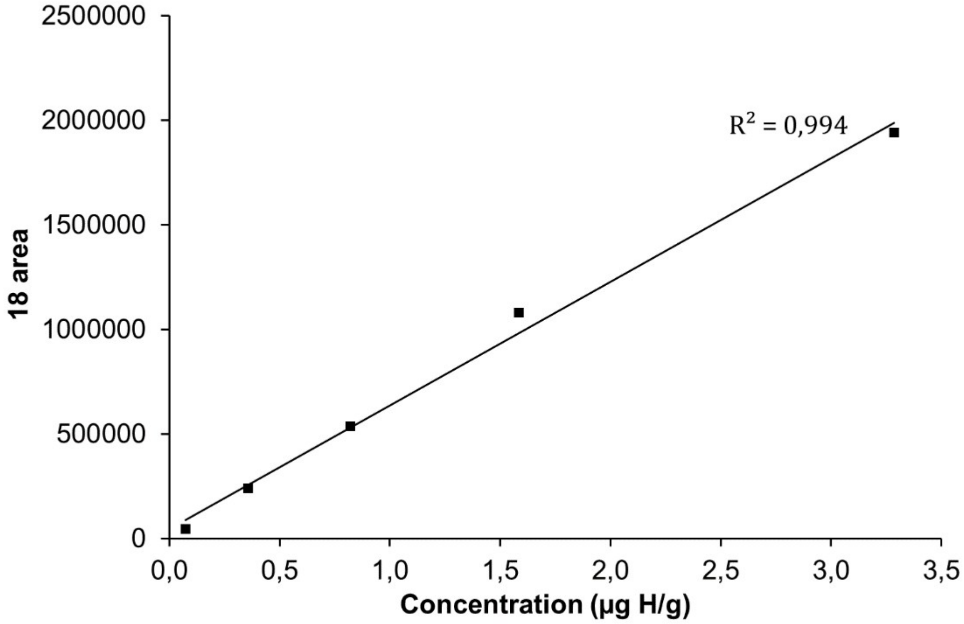


Figure S10. Linearity for acenaphthene from 0.020 to 3 µg H g^{-1} using 925°C and 0.4 mLmin^{-1} O_2/He.

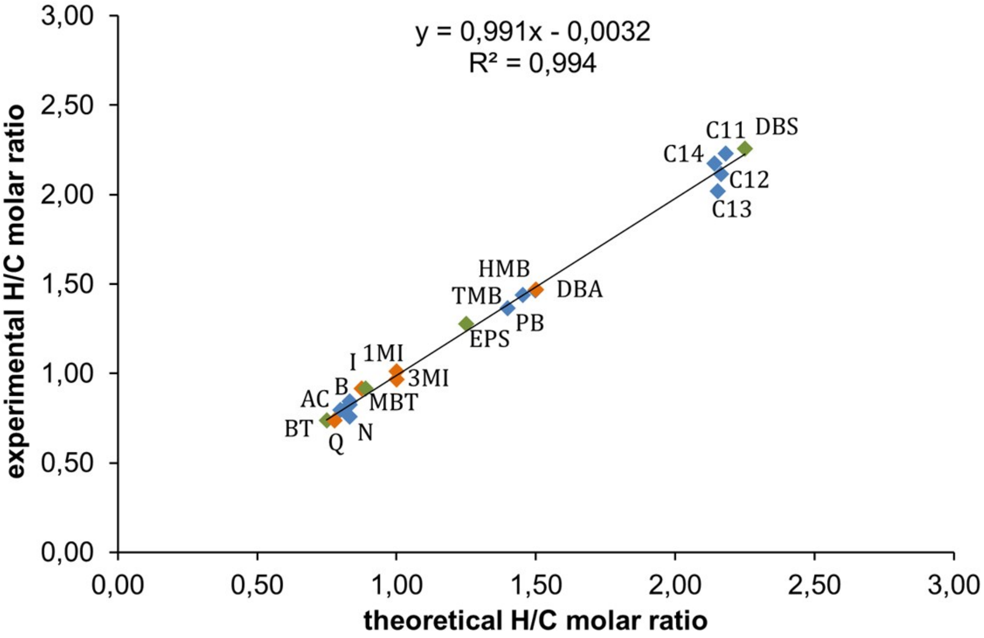


Figure S11. Experimental H/C molar ratio against theoretical H/C molar ratio for a mixture of organic compounds without heteroatoms (in blue: C11 - undecane, C12 - dodecane, C13 - tridecane, C14 - tetradecane, PB - pentamethylbenzene, B - biphenyl, HMB - hexamethylbenzene, TMB - tetramethylbenzene, AC - acenaphthene, N - naphthalene), S-containing compounds (in green: DBS - dibutyl sulfide, EPS - ethyl phenyl sulfide, BT - benzothiophene, MBT - 3-Methylbenzothiophene) and N-containing compounds (in orange: Q - quinoleine, 1MI - 1-Methylindole, I - indole, 3MI - 3-Methylindole).

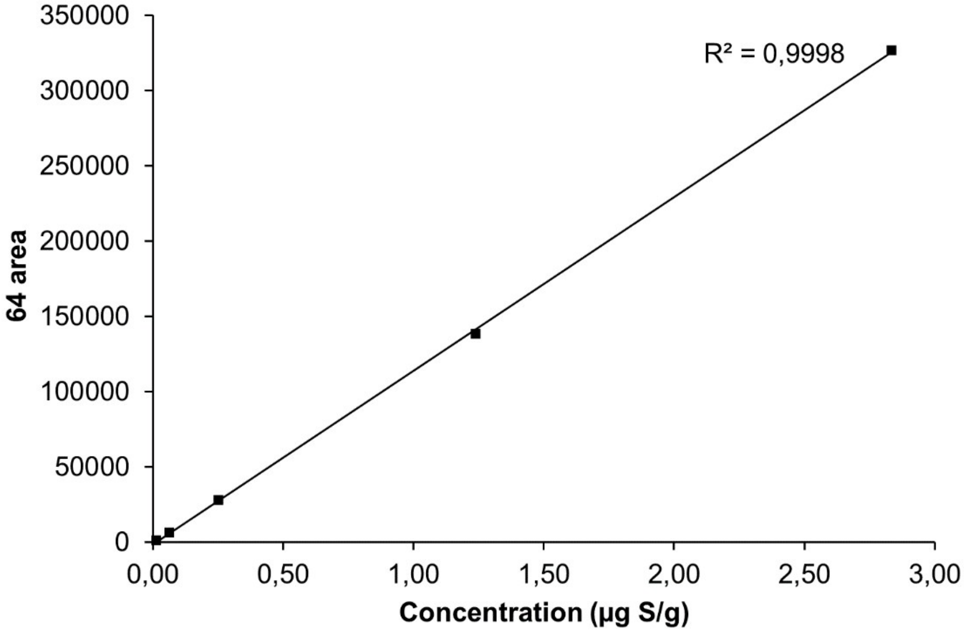


Figure S12. Linearity for 3-Methylbenzothiophene from 0.013 to 2.8 µg S g^{-1} using 925°C and 0.4 $mLmin^{-1}$ O_2/He.

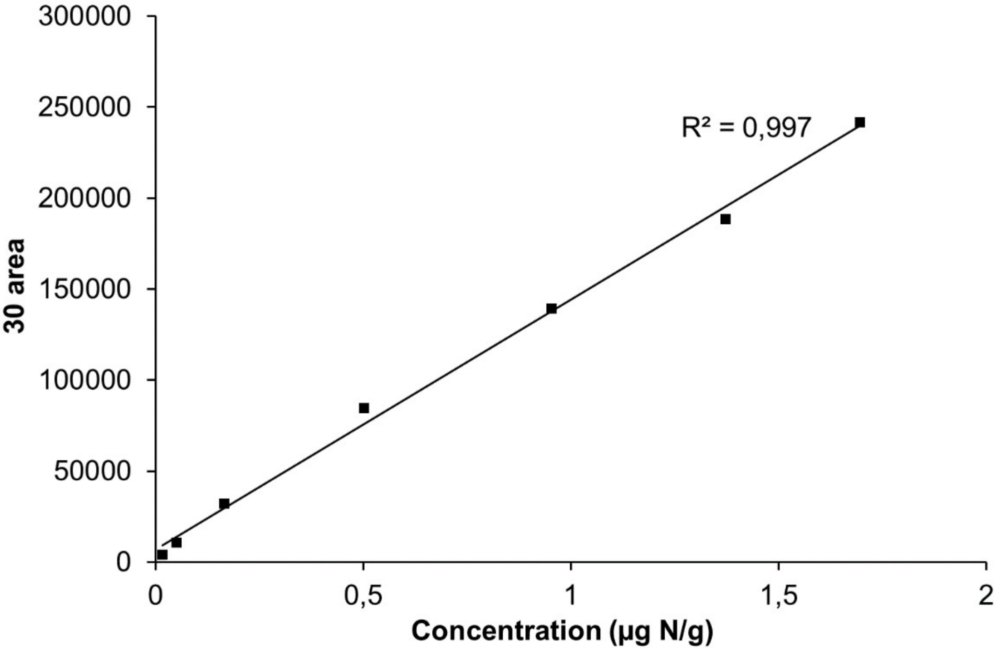


Figure S13. Linearity for indole from 0.016 to 1.7 µg N g^{-1} using 1150°C and 0.4 $mLmin^{-1}$ O_2/He.

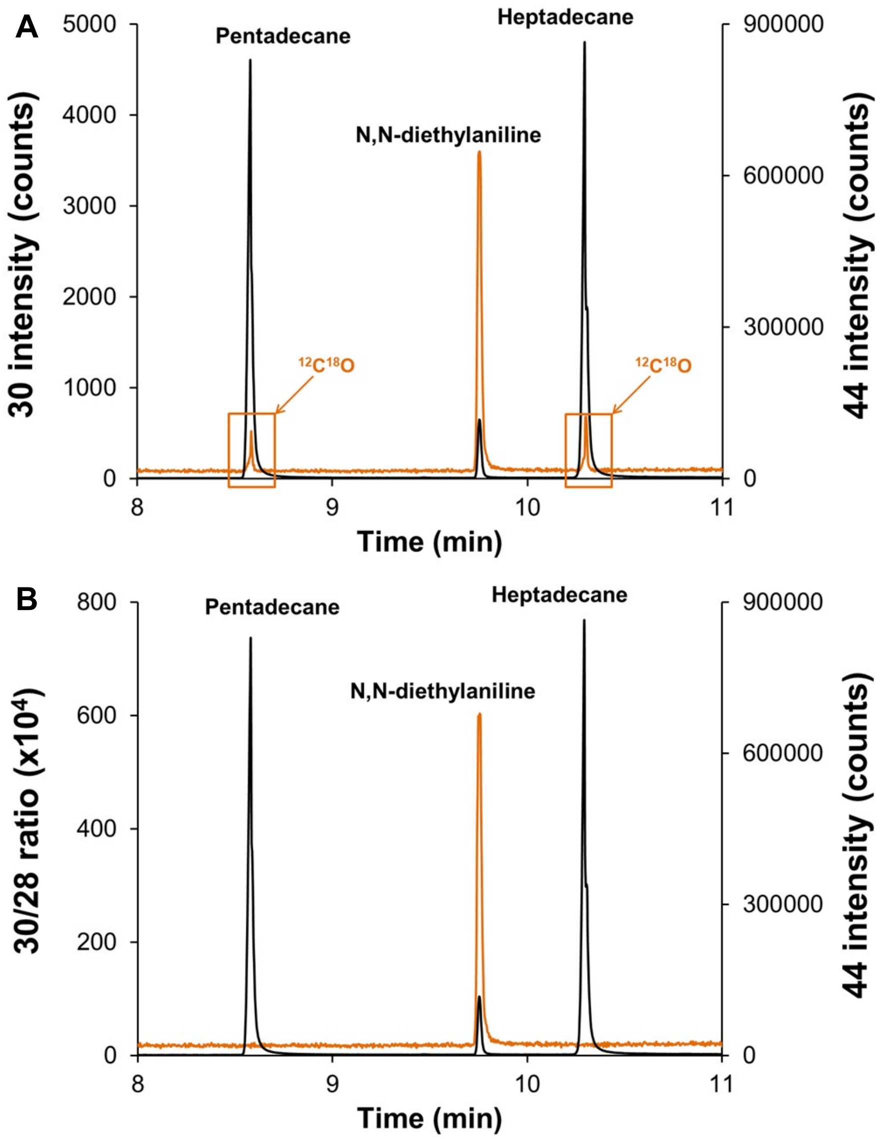


Figure S14. Chromatogram for a mixture of two alkanes (pentadecane and heptadecane, ca. 16 µg C g^{-1}) and N,N-diethylaniline (ca. 1 µg C g^{-1} and 0.2 µg N g^{-1}). A) Signals at m/z 44 and 30 correspond to CO_2 and NO, respectively. Interference (unspecific) signal at m/z 30 observed for the alkanes corresponds to the $^{12}C^{18}O$ contribution due to the CO_2 degradation at the ion source. Using the response factor obtained from the N,N-diethylaniline, it can be estimated that such signals would correspond to a concentration of nitrogen of ca. 0.016 µg N g^{-1}. B) 30/28 and 44 signals. As can be seen, after normalization with the 28 signal (coming from the isotopologue $^{12}C^{16}O$ of the interference $^{12}C^{18}O$), the new 30/28 signal becomes specific of the N presence. As a matter of fact, the interference at 30 for the high concentrated alkanes disappears completely in the new 30/28 profile.

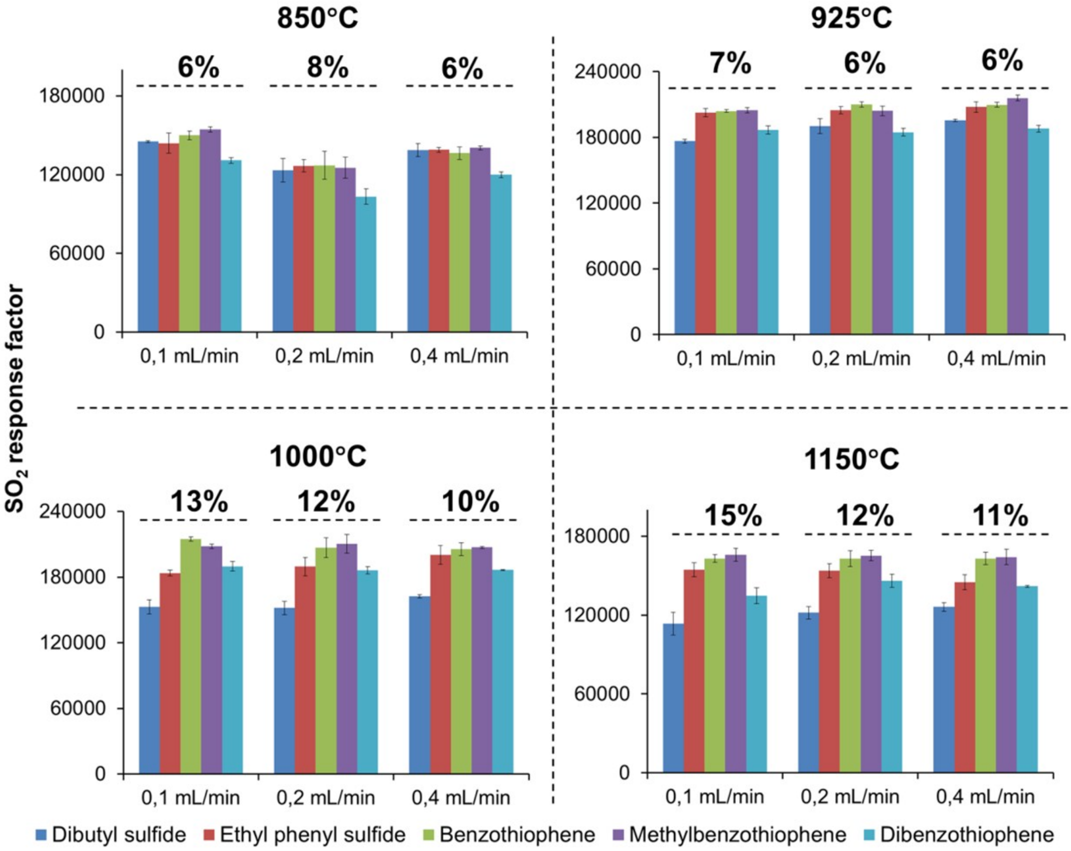


Figure S15. SO_2 response factors (peak area at m/z 64 divided by the S concentration in the corresponding compound) obtained for the mixture of S-containing compounds (2 µg S g^{-1}) at different temperatures (ranging from 850 to 1150°C) and O_2/He flows (0.1-0.4 $mLmin^{-1}$). Error bars indicate 1 SD (n=3). RSD of the different response factors obtained for the mixture of compounds under the different conditions assayed are given.

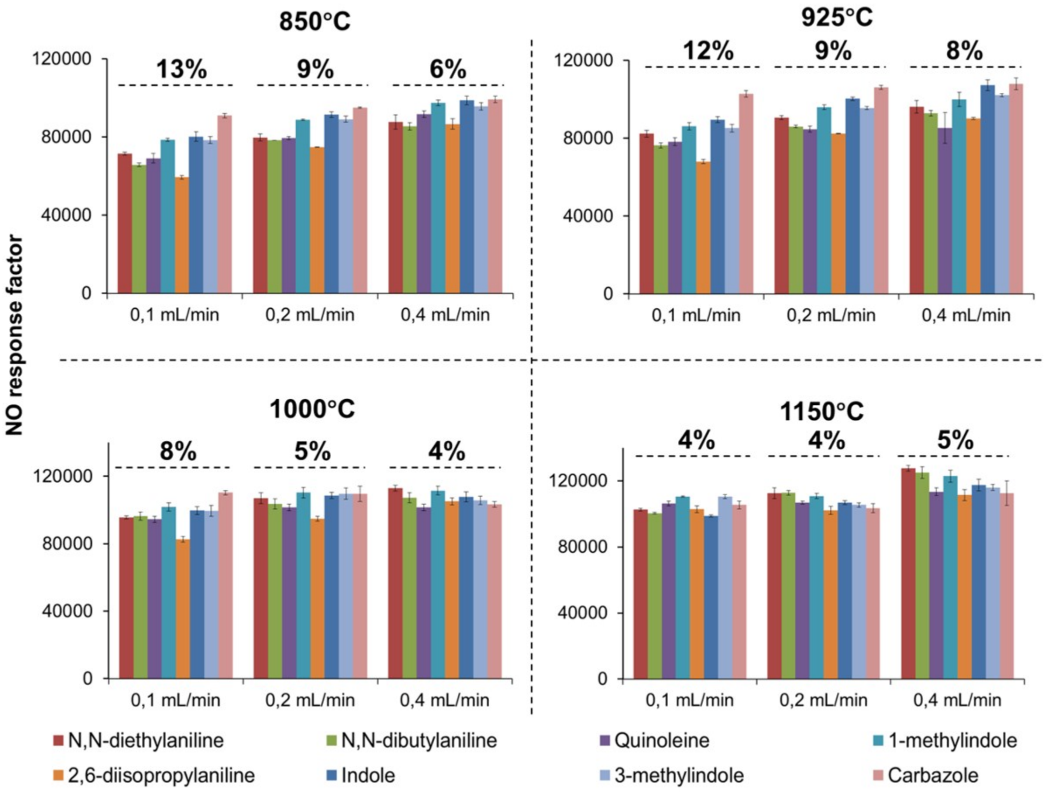


Figure S16. NO response factors (peak area at m/z 30 divided by the N concentration in the corresponding compound) obtained for the mixture of N-containing compounds (1 µg N g^{-1}) at different temperatures (ranging from 850 to 1150°C) and O_2/He flows (0.1-0.4 mLmin^{-1}). Error bars indicate 1 SD (n=3). RSD of the different response factors obtained for the mixture of compounds under the different conditions assayed are given.

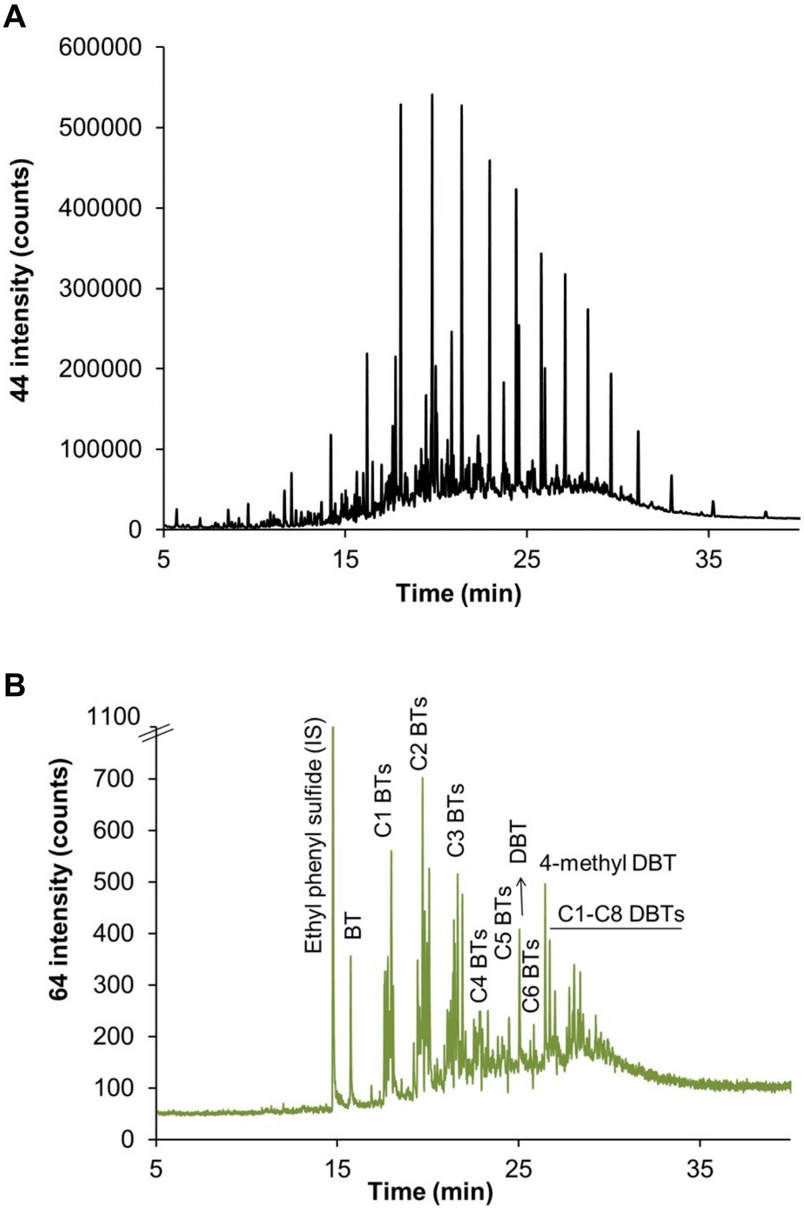


Figure S17. Chromatogram for the diesel sample (ca. 4000 µg S g^{-1}) diluted 1:800 and spiked with ethyl phenyl sulfide as internal standard; A) m/z 44 and B) m/z 64.

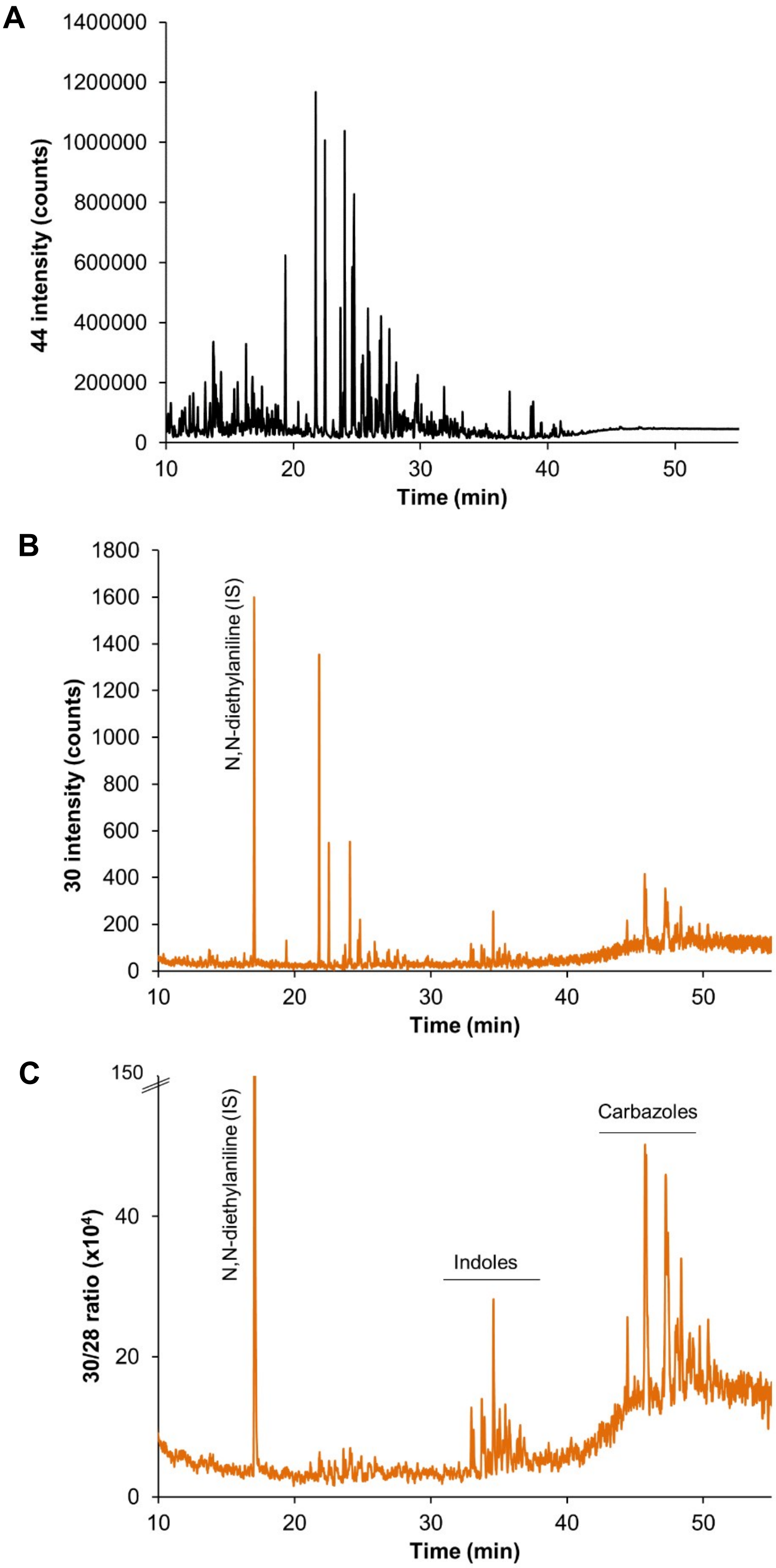


Figure S18. Chromatogram for the diesel sample (ca. 400 µg N g-1) diluted 1:500 with the internal standard (N,N-diethylaniline, 0.25 µg N g^{-1}) A) m/z 44, B) m/z 30 (not corrected for $^{12}C^{18}O$ contribution), C) complete N-selective 30/28 profile (corrected for the unspecific $^{12}C^{18}O$ contribution, see Fig S13)

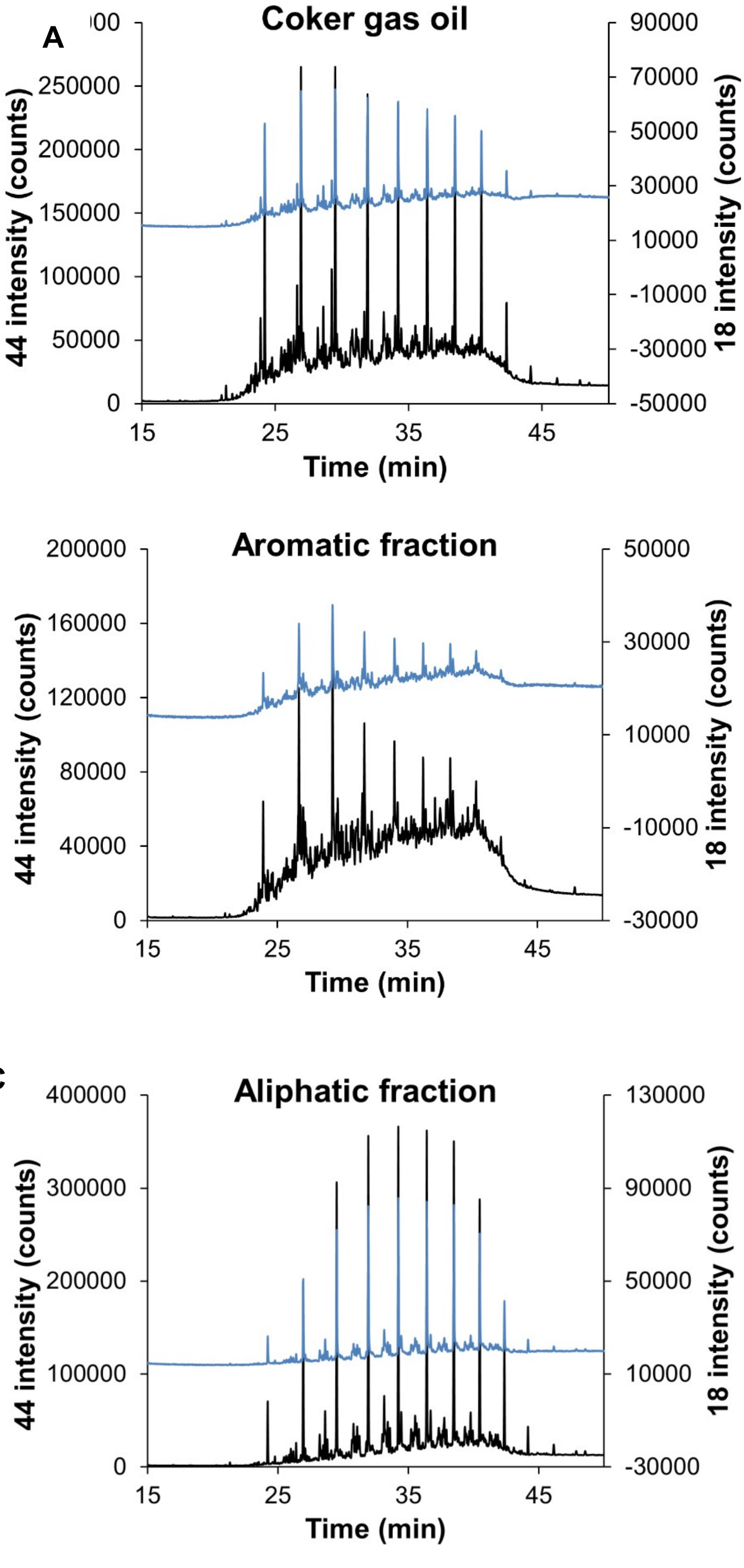


Figure S19. Chromatogram for m/z 44 (C, black line) and m/z 18 (H, blue line) for the original coker gas oil sample (A) and its aromatic (B) and aliphatic (C) fractions.

Table S3. Elemental composition (μg element g^{-1}, n=3) obtained for S- and N-containing compounds using benzothiophene or 1-Methylindole as corresponding generic IS, respectively. Uncertainty corresponds to 1 SD. Concentrations (μg compound g^{-1}) of the injected compounds were: Dibutyl sulfide: 9.6 μg g^{-1}; Ethyl phenyl sulfide: 10.8 μg g^{-1}; Methylbenzothiophene: 9.6 μg g^{-1}; Dibenzothiophene: 9.7 μg g^{-1}; N,N-Diethylaniline: 6.3 μg g^{-1}; N,N-Dibutylaniline: 6.6 μg g^{-1}; Quinoleine: 6.6 μg g^{-1}; 2,6-Diisopropylaniline: 7.2 μg g^{-1}; Indole: 6.8 μg g^{-1}; 3-Methylindole: 5.9 μg g^{-1}; Carbazole: 6.4 μg g^{-1}.

Compound	Carbon	Hydrogen	Sulfur	Nitrogen
Dibutyl sulfide	6.5 ± 0.2 (103±3%)	1.22 ± 0.04 (104±4%)	2.14 ± 0.08 (102±4%)	
Ethyl phenyl sulfide	7.8 ± 0.2 (105±2%)	0.85 ± 0.02 (109±2%)	2.54 ± 0.09 (102±4%)	-
Methylbenzothiophene	7.3 ± 0.1 (103±2%)	0.52 ± 0.02 (99±3%)	2.15 ± 0.10 (103±5%)	-
Dibenzothiophene	6.7 ± 0.1 (89±2%) (102±3%)*	0.37 ± 0.01 (87±2%) (99±5%)*	1.48 ± 0.03 (88±2%) (101±5%)*	-
N,N-Diethylaniline	5.22 ± 0.06 (103±1%)	0.67 ± 0.01 (106±2%)	-	0.62 ± 0.01 (106±2%)
N,N-Dibutylaniline	5.48 ± 0.03 (101±1%)	0.75 ± 0.02 (102±1%)	-	0.46 ± 0.01 (102±1%)
Quinoleine	5.13 ± 0.04 (94±1%)	0.32 ± 0.01 (91±2%)	-	0.66 ± 0.01 (91±2%)
2,6-Diisopropylaniline	5.79 ± 0.01 (99±1%)	0.78 ± 0.01 (101±1%)	-	0.52 ± 0.01 (101±2%)
Indole	5.70 ± 0.02 (102±1%)	0.41 ± 0.01 (101±2%)	-	0.78 ± 0.02 (101±1%)
3-Methylindole	5.06 ± 0.07 (104±1%)	0.41 ± 0.01 (101±5%)	-	0.60 ± 0.01 (101±5%)
Carbazole	5.16 ± 0.06 (94±1%)	0.34 ± 0.01 (98±4%)	-	0.49 ± 0.02 (98±4%)
Mean	101*%	100*%	102*%	100*%

*Values obtained when using BD-EN14103 column

Table S4. Critical comparison of the analytical features of the detection method presented here with other established detectors in GC for hydrogen, nitrogen and sulfur.

Detector	DL for H	DL for N	DL for S	Reference
SCD	-	-	3 pg	Anal. Methods, 2016, 8, 7014–7024
NCD	-	2 pg	-	J. Chromatogr. A, 2012, 1219, 180–187
PFPD	-	-	3 pg	J. Chromatogr. A, 2006, 1136, 89–98
AED*	11 pg	12 pg	3 pg	Fresenius J Anal Chem, 1997, 357, 1133—1141
ICP-MS/MS	-	-	0.3 pg	Anal. Chem. 2019, 91, 7019−7024
GC-combustion-MS	5 pg	0.7 pg	0.7 pg	This publication

*Please note that AED suffers from significant quenching effects in the analysis of complex unresolved samples. Furthermore, simultaneous analysis of C, H, S and N cannot be performed with regular AED instrument becuase it allows multiplexed monitoring of several emission lines only when they fall within the spectral region covered by the photodiode-array spectrometer (typically a window of 20–25 nm). This is the case of H, whose detection wavelength (486 nm), falls out of the window created for simultaneous C, S and N detection (typically detected at 193, 181 and 174 nm, respectively).

Table S5. Quantification of total sulfur content and some major species and families in the diesel sample by GC-combustion-MS (2 SD, n=3). Concentrations are given in µg S g^{-1}. Total sulfur content determined by X-ray fluorescence method is also given.

Total content by X-ray method	3900 ± 110
GC-combustion-MS	
Total analysis	3743 ± 216
Individual species	
Benzothiophene	49 ± 2
Dibenzothiophene	83 ± 12
4-Methylbenzothiophene	89 ± 15
Families	
C1 benzothiophenes	300 ± 26
C2 benzothiophenes	458 ± 60
C3 benzothiophenes	489 ± 50
C4 benzothiophenes	230 ± 14
C5 benzothiophenes	361 ± 26
C6 benzothiophenes	166 ± 26
C1-C8 dibenzothiophenes	1397 ± 176

Table S6. Quantification of total nitrogen content and some major families in the diesel sample by GC-combustion-MS (2 SD, n=3). Concentrations are given in µg N g^{-1}. Total nitrogen content determined by chemoluminiscence method is also given.

Total content by chemoluminiscence	497 ± 10
GC-combustion-MS	
Total analysis	524 ± 22
Families	
Indoles	111 ± 8
Carbazoles	368 ± 25

Table S7. H/C molar ratios for the coker gas oil sample and its corresponding aliphatic and aromatic fractions. Experimental H_2O/CO_2 ratios obtained which could be converted into H/C molar ratios using generic standards (given in Figure S9) are also given

Sample	18/44 experimental ratio	Calculated H/C molar ratio
Coker gas oil	0.15	1.46
Aromatic fraction	0.13	1.32
Aliphatic fraction	0.20	1.99