Supplementary information

Table S1. Analytes, internal standards and surrogates employed for DTD- and IDTD-GC-TOFMS. A surrogate is only specified when no native standard was available for calibration. Thus, only semi-quantification was achievable for these analytes. Benzofluoranthenes were not chromatographically separated (sum of benzo[b]-, benzo[j]- and benzo[k]fluoranthene).

Analyte	Internal Standard	Surrogate	m/z used for quanti-fication	Concentration of internal standard [ng]
Phenanthrene	Phenanthrene-d_{10}		178 / 188	3.45
Anthracene	Anthracene-d_{10}		178 / 188	0.461
Fluoranthene	Fluoranthene-d_{10}		202 / 212	0.681
Pyrene	Pyrene-d_{10}		202 / 212	1.68
Benzo[a]anthracene	Benzo[a]anthracene-d_{12}		228 / 240	0.962
Chrysene	Chrysene-d_{12}		228 / 240	0.962
sum Benzofluoranthenes	Benzo[b]fluoranthene-d_{12}	Benzo[b]-fluoranthene	252 / 264	0.802
Benzo[e]pyrene	Benzo[e]pyrene-d_{12}		252 / 264	0.802
Benzo[a]pyrene	Benzo[a]pyrene-d_{12}		252 / 264	1.04
Perylene	Perylene-d_{12}		252 / 264	1.12
Indeno[1,2,3-cd]pyrene	Indeno[1,2,3-cd]pyrene-d_{12}		276 / 288	0.721
Dibenzo[ah]anthracene	Dibenzo[ah]anthracene-d_{14}		278 / 292	0.842
Benzo[ghi]perylene	Benzo[ghi]perylene-d_{12}		276 / 288	2.00
Coronene	Coronene-d_{12}		300 / 312	0.641
9H-Fluoren-9-one	Phenanthrene-d_{10}		180 / 188	3.45
9,10-Anthracenedione	9,10-Anthracenedione-d_8		180 / 188	1.89
1,8-Naphthalic anhydride	9,10-Anthracenedione-d_8		154 / 162	1.89
Cyclopenta[def]-phenanthrenone	Benzo[a]anthracene-d_{12}		204 / 240	0.962

11H-Benzo[a]fluoren-11-one	Benzo[a]anthracene-d_{12}		230 / 240	0.962
11H-Benzo[b]fluoren-11-one	Benzo[a]anthracene-d_{12}		230 / 240	0.962
Benzo[a]anthracene-7,12-dione	Benzo[a]anthracene-7,12-dione-d_{10}		258 / 268	1.92
Malic acid	Palmitic acid-d_{31}		233 / 344	60.8
Vanillin	Vanillin-$^{13}C_6$		194 / 200	15.6
Galactosan	Levoglucosan-$^{13}C_6$		217 / 220	60.8
Mannosan	Levoglucosan-$^{13}C_6$		217 / 220	60.8
Levoglucosan	Levoglucosan-$^{13}C_6$		217 / 220	60.8
Phthalic acid	Levoglucosan-$^{13}C_6$		295 / 338	60.8
Vanillic acid, methyl ester	Vanillin-$^{13}C_6$		224 / 200	12.6
Vanillic acid	Palmitic acid-d_{31}		297 / 344	12.6
Syringic acid	Palmitic acid-d_{31}		327 / 344	12.6
Syringyl aldehyde	Palmitic acid-d_{31}	Aceto-syringone	224 / 344	12.6
Acetosyringone	Palmitic acid-d_{31}		238 / 344	12.6
Syringylacetone	Levoglucosan-$^{13}C_6$		239 / 338	60.8
Retene	Benzo[a]anthracene-d_{12}	Benzo[a]-anthracene	219 / 240	0.962
Isopimaric acid	Benzo[a]anthracene-d_{12}		241 / 240	0.962
Dehydroabietic acid methyl ester	Pyrene-d_{10}	Pyrene	299 / 212	1.68
Dehydroabietic acid	Pyrene-d_{10}	Isopimaric acid	239 / 212	1.68
Abietic acid	Palmitic acid-d_{31}		256 / 344	12.6
7-Oxodehydroabietic acid	Benzo[a]anthracene-d_{12}	Isopimaric acid	253 / 240	12.6
Divanillyl	Pyrene-d_{10}	Pyrene	239 / 212	1.68

Table S2. Validation parameters obtained from the calibration curves of SE-GC-TOFMS. Calibration range means lowest and highest standard concentrations used for the calibration curve; a = interception, b = slope (area ratio / mass ratio). The limit of quantification (LOQ) of the method is defined as the minimum amount of substance that is according to the minimum reliable signal plus nine times (three times for LOD) the standard deviation of this underground signal.

Analyte	Calibration range [ng]	a	b	R^2	Precision	LOQ per sample [ng]
Phenanthrene	0.790 - 39.5	-0.048	1.190	1.000	2%	0.045
Anthracene	0.212 - 10.6	-0.353	1.542	0.991	10%	0.018
Fluoranthene	0.283 - 14.1	-0.112	1.384	0.996	6%	0.027
Pyrene	0.392 - 19.6	0.003	1.345	0.997	6%	0.026
Benzo[a]anthracene	0.290 - 14.5	0.107	1.461	0.995	8%	0.049
Chrysene	0.277 - 13.8	-0.002	0.549	0.998	5%	0.043
sum Benzofluoranthenes	0.098 - 4.89	-0.070	0.778	0.995	7%	0.060
Benzo[e]pyrene	0.134 - 6.71	-0.147	1.601	0.994	7%	0.044
Benzo[a]pyrene	0.130 - 6.49	-0.082	1.359	0.991	8%	0.073
Perylene	0.070 - 3.52	-0.135	1.313	0.984	12%	0.059
Indeno[1,2,3-cd]pyrene	0.069 - 3.44	-0.051	0.793	0.998	6%	0.150
Dibenzo[ah]anthracene	0.072 - 3.60	-0.099	1.394	0.948	14%	0.110
Benzo[ghi]perylene	0.073 - 3.63	-0.058	1.952	0.998	5%	0.063
Coronene	0.072 - 3.60	-0.323	1.298	0.996	6%	0.109
9H-Fluoren-9-one	0.362 - 18.1	-0.058	0.524	0.998	5%	0.063
9,10-Anthracenedione	0.280 - 14.0	-0.100	0.548	0.997	6%	0.403
1,8-Naphthalic anhydride	0.414 - 20.7	-1.115	0.327	0.969	9%	0.716
Cyclopenta[def]-phenanthrenone	0.075 - 3.74	-0.123	0.932	0.985	15%	0.099
11H-Benzo[a]fluoren-11-one	0.081 - 4.06	-0.018	0.204	0.987	13%	0.442
11H-Benzo[b]fluoren-11-one	0.079 - 3.93	-0.045	0.580	0.982	18%	0.172
Benzo[a]anthracene-7,12-dione	0.37 - 18.5	-0.866	2.631	0.991	9%	0.108

Malic acid	0.976 - 97.6	-0.033	0.228	0.995	10%	2.976
Vanillin	0.057 - 5.67	0.004	1.353	0.999	4%	0.229
Galactosan	0.221 - 22.1	-0.054	5.112	0.990	14%	0.024
Mannosan	1.05 - 105	-0.009	1.200	0.996	9%	0.090
Levoglucosan	3.42 - 342	-0.003	0.558	0.999	4%	0.168
Phthalic acid	0.604 - 60.4	-0.014	0.376	0.994	12%	0.302
Vanillic acid methyl ester	0.054 - 5.44	-0.043	6.836	0.997	10%	0.052
Vanillic acid	0.054 - 5.38	0.005	4.595	0.998	4%	0.139
Syringic acid	0.053 - 5.34	-0.028	3.504	0.998	6%	0.175
Syringyl aldehyde	0.036 - 3.64	-0.001	3.941	0.989	9%	0.265
Acetosyringone	0.036 - 3.64	-0.001	3.941	0.989	9%	0.265
Syringylacetone	1.17 - 117	-0.018	0.307	0.995	10%	0.356
Retene	0.290 - 14.5	-0.653	2.035	0.982	19%	0.049
Isopimaric acid	0.142 - 14.2	0.058	0.237	0.996	6%	0.418
Dehydroabietic acid, methyl ester	0.392 - 19.6	-0.047	1.432	1.000	3%	0.026
Dehydroabietic acid	0.392 - 19.6	0.005	0.107	0.997	5%	0.026
Abietic acid	0.022 - 2.20	0.007	0.564	0.938	9%	0.159
7-Oxodehydroabietic acid	0.142 - 14.2	0.058	0.237	0.996	6%	0.418
Divanillyl	0.392 - 19.6	-0.047	1.432	1.000	3%	0.026

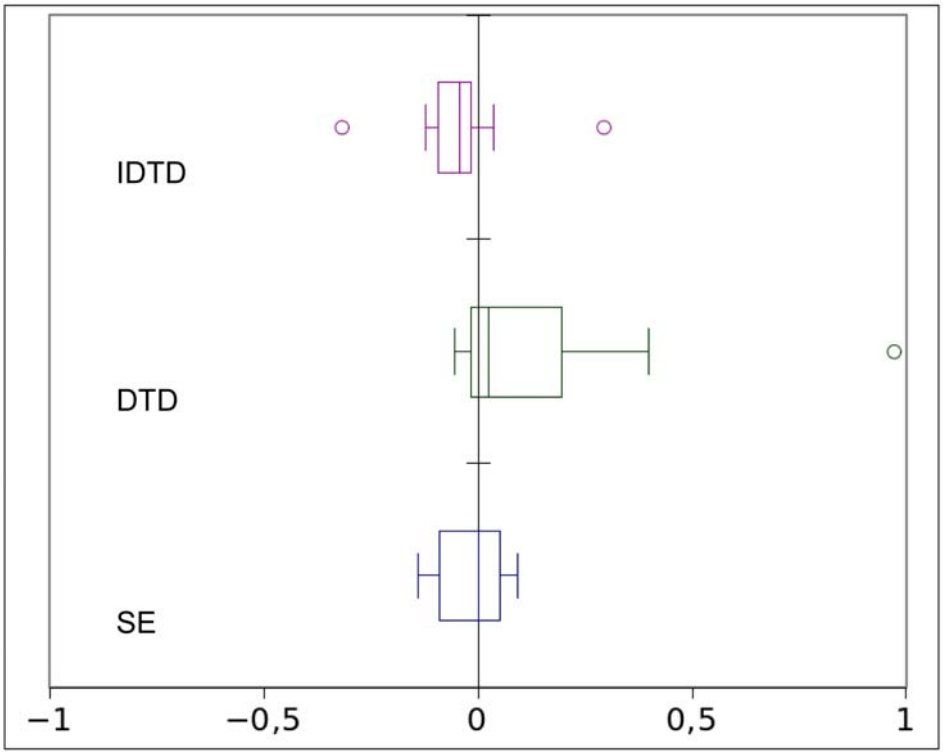

Figure S1. Box plots for visualization of variations of the different methods applied to Standard Reference Material Urban Dust 1649a. The zero point on the scale refers to the certified values normalized to zero. Variations are calculated relative to the normalized certified values (1 = 100 %). The extreme outliers of the results of anthracene and dibenzo[ah]anthracene are not visualized.