

CHARACTERISATION OF AEROSOL PARTICLES USING COMBINED THERMOANALYTICAL TECHNIQUES

G. Matuschek^{1*}, *Y. Saritas*¹, *E. Karg*² and *A. Schroepel*²

¹GSF-National Research Center for Environment and Health, Institute of Ecological Chemistry, Focus Network Aerosols and Health, P.O. Box 1129, D-85758 Oberschleißheim, Germany

²GSF-National Research Center for Environment and Health, Institute of Inhalation Biology, P.O. Box 1129, D-85758 Oberschleißheim, Germany

Abstract

Four different artificial aerosol particles as well as one standard environmental aerosol particle (NIST SRM 1649a) were investigated. While the mass loss of the aerosol particles varies from 1.5 to 32% of the entire mass, only a small part of each volatile fraction consists of organic compounds. Due to the construction of the combined thermoanalytical system, only a small part of the evolved gases is used for the mass spectrometric investigation. This results in a restricted sensitivity which does not allow an identification of individual organic components. Additional investigations like thermal desorption GC-MS reveal up to 1600 individual components (SRM 1649a).

Keywords: aerosols, GC-MS, mass spectrometry, thermal analysis

Introduction

Combined thermoanalytical techniques have widely been used for the characterization of various materials. In the last years, besides others, applications in the field of polymers [1–3], metal complexes with organic ligands [4–8], asphaltenes [9] and coals [10–12] have been published. The aim of this study was to test the usability of thermal analysis coupled to mass spectrometry for the investigation of artificial and environmental aerosol particles. Besides the aesthetic problem of 'dirty fog' in the atmosphere particulate matter pollution influences the human health. Epidemiological and experimental data have revealed a correlation between human respiratory problems and the concentration of ambient fine and ultra-fine particles in urban air [13–15]. Moreover, recent epidemiological studies have suggested that an increase in the concentration of inhaled particles of about $10 \mu\text{g m}^{-3}$ is associated with a 1% increase in premature mortality [12, 16] and from the coronary event registry Augsburg with about 800 cases is associated with a 10% increase of risk to myocardial infarction. Fine and ultra-fine aerosol particles can be transported long distances and reach deep into the lung. They can be enriched in toxic, mutagenic and carcinogenic components. Due to this potential health impact, PM 10 (particulate matter with diame-

* Author for correspondence: E-mail: matuschek@gsf.de

ter < 10 μm) has been widely studied. Due to the interaction of particles with their environment, environmental aerosol particles are loaded with chemicals. The central aim of the biomedical aerosol research is the study of the distribution, deposition and retention of inhaled aerosol particles in the lung and their effect on the lung functions as well as on the cardio-vascular system. For this purpose, the characterisation of the aerosol particles and the identification and quantification of chemical stressors located on the aerosol particles (chemical load) is an essential contribution to the impact research.

The aim of this study was to identify the organic load of artificial carbonaceous particles used for toxicological studies as well as to determine the organic load of an urban aerosol.

Experimental

The thermoanalytical investigations were carried out using a Netzsch STA 409 thermal analyser coupled to a Balzers quadrupole mass spectrometer by a so-called skimmer[®] system. The samples were introduced without any pre-treatment and heated in nitrogen atmosphere with a heating rate of 10 K min^{-1} . Mass spectra were taken every 10 K. Additional thermal desorption GC/MS investigations were performed using a double shot pyrolyser system from Frontier Lab Inc. with an Agilent 6890 GC/MS system. The artificial model aerosol particles were produced using a CAST (Combustion Aerosol Standard) generator. This generator produces soot model particles by a diffusion flame. The organic carbon content of these particles can be controlled by the fuel gas flow rate and the N_2/O_2 gas flow rate.

Results

The aim of this study was to identify the organic load of artificially created carbonaceous particles as well as of environmental aerosols. For this purpose four artificial carbonaceous particles, produced by the CAST system and a standard reference material from the US National Institute of Standards and Technology (NIST) SRM 1649a (urban dust) were investigated.

Thermal analysis / mass spectrometry

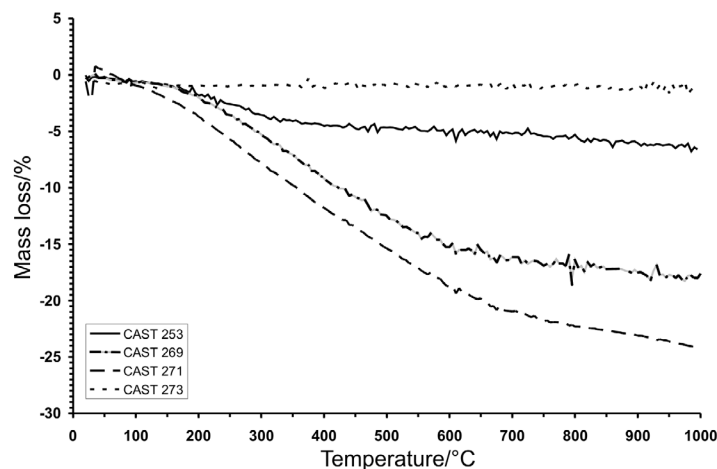
Artificial model aerosol particles (CAST)

The thermal treatment (thermal desorption) of the CAST particles revealed for all particles a mass loss from room temperature up to 1000°C. As shown in Fig. 1 it varies with the different particle types and can be up to 24% of the entire particle mass. In aerosol science, the organic matter (OM) is often defined as the volatile substances (except water and CO_2) up to 350°C. For this reason, the mass loss was calculated from the TG curve at this temperature. The different mass losses are given in Table 1.

The four different CAST particles are different in their desorption behaviours. CAST 273 gives a mass loss of about 1 to 1.5% in the temperature range at about 100°C.

Table 1 Calculated mass losses of CAST particles

	Type			
	CAST 253/%	CAST 269/%	CAST 271/%	CAST 273/%
350°C	-4.2	-8	-10.5	-1
Total	-6.6	-18	-24.1	-1.5

**Fig. 1** TG curves of CAST particles in nitrogen atmosphere, heating rate 10 K min^{-1}

It can be assumed, that this is most probably due to the evaporation of moisture from the particles. The other three samples show a greater mass loss in the higher temperature range starting at about 150°C and ending depending on the mass loss at ca. 350 , 700 and 850°C . The corresponding total ion currents of the on-line measured mass spectral data registered during the thermal desorption process are given in Fig. 2.

Again, CAST 273 shows a different behaviour than the other three samples. The total ion current did not show a distinct evolution maximum at any temperature. The other samples show two distinct maxima. The first maximum occurs in the region below or around 100°C and a second one can be detected around 250 – 350°C . Since it can be assumed that the first maximum is probably due to the evolution of moisture, the second maximum might indicate the evolution of organic substances loaded on the particles surface. The summarized mass spectra from room temperature up to 350°C in Fig. 3 confirm this assumption and give a more detailed view on the evolution of organic compounds. In the lower mass region with the highest intensities, CAST 273 shows besides the typical fragmentation pattern of water (m/z 16, 17 and 18) peaks at m/z 15, 26, 30 and 44. These peaks can be due to the evolution of CO_2 or C_3H_8 (m/z 44), C_2H_6 (m/z 30) and CH_3^+ (m/z 15) as a fragment from the two other organic components. From CAST 271 the fragments at m/z 12, 18, 26 and 44 show the highest abundance. Since in this case the fragmentation pattern of water can not be observed, m/z 18 must be explained from another source, which might be a C_3^{2+} cluster.

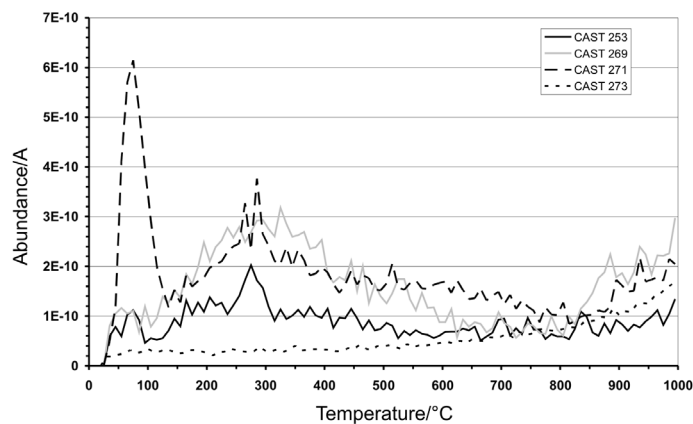


Fig. 2 Total ion currents of the investigations of CAST particles

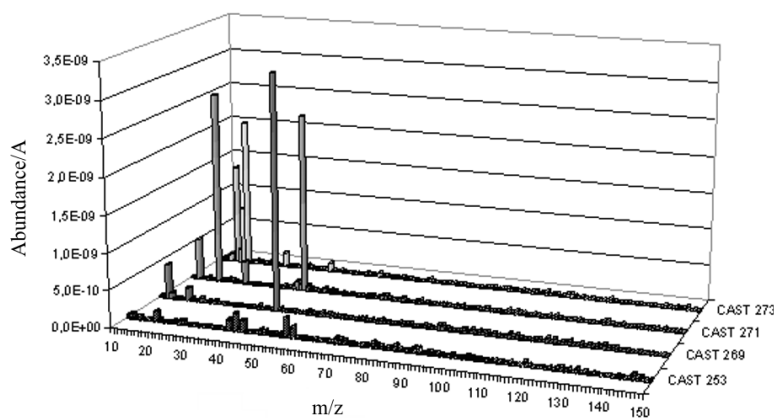


Fig. 3 Summarized mass spectra (RT – 350°C) of the investigation of CAST particles

The ions at m/z 44, 26 and 12 can be explained as CO_2 or C_3H_8 , C_2H_2 and carbon. CAST 269 shows besides a strong peak at m/z 44 and 12 a smaller one at m/z 18. Due to the low abundance of this ion, no clear assignment to water or the C_3 cluster is possible. The missing m/z 15 supports the assignment of CO_2 to m/z 44 and m/z 12 as its fragment. CAST 253 seems to be clearly loaded with organic compounds. Significant peaks at m/z 13, 39, 41, 43, 55, 57, 70, 91 and 128 show the typical pattern of the release of aromatic and non aromatic organic substances.

A closer view to the higher mass region (50–150 amu) reveals more details (Fig. 4). From this figure, the evolution of organic components for all of the samples can be detected. Since CAST 253 shows the highest abundant fragments for all samples, the highest organic load of the particles within the series of samples can be assumed. Concluding for the CAST samples, the different types show different behaviour and composition.

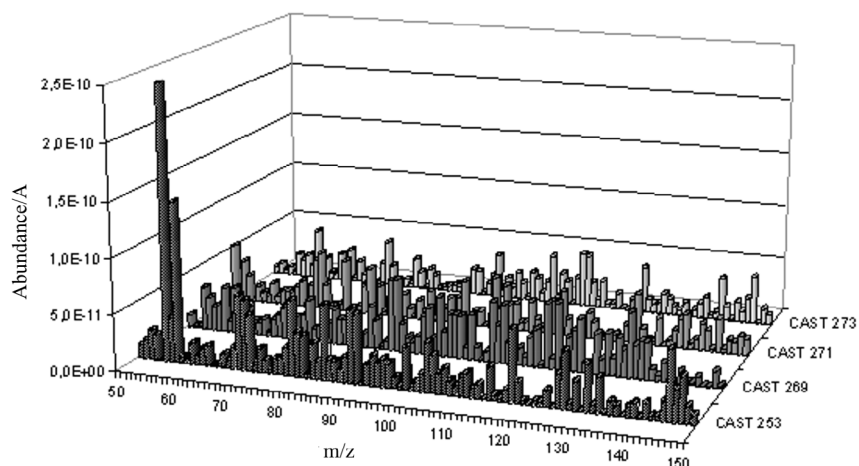


Fig. 4 Summarized mass spectra (RT – 350°C) of the investigation of CAST particles

- CAST 253: These particles are loaded by a high amount of organic components. Since no other significant fragments were detected, the entire mass loss of 6% can be assumed to be organic load.
- CAST 269: These particles are also loaded by organic compounds, but not in that high amount as CAST 253. A great part of the detected mass loss is due to the evolution of CO₂.
- CAST 271: Besides a small organic load, the evolution of CO₂ and small, unsaturated organic components (C₂H₂) are responsible for the detected mass loss. Since the evolution of these small components occurs in the higher temperature region, a cleavage from the particle core can be assumed preferably to a physical adsorption of these components.
- CAST 273: The greatest part of the mass loss of 1–1.5% of these particles can be explained by the evolution of moisture in the lower temperature region. Nevertheless, a small part is also due to the organic components, adsorbed on the particles surface.

SRM 1649a (urban dust)

Besides the artificial aerosol particles, a real sample (urban dust SRM 1649a, NIST) was also investigated to compare the artificial particles to an environmental aerosol. The thermoanalytical investigations of the real sample showed a quite different behaviour of the sample compared to the artificial particles. Under thermal treatment, the mass loss up to 1000°C occurred in several steps to 32% (Fig. 5). In the range up to 350°C a mass loss of about 18% was observed.

The reconstructed ion currents in the low mass region (m/z 10–50) and the high mass region (m/z 50–250) show several peaks (cf. Fig. 6). In the low mass region there are 5 maxima at 100, 150, 290, 400 and 750°C, while the high mass region only two peaks at 290 and 420°C with lower intensities were observed.

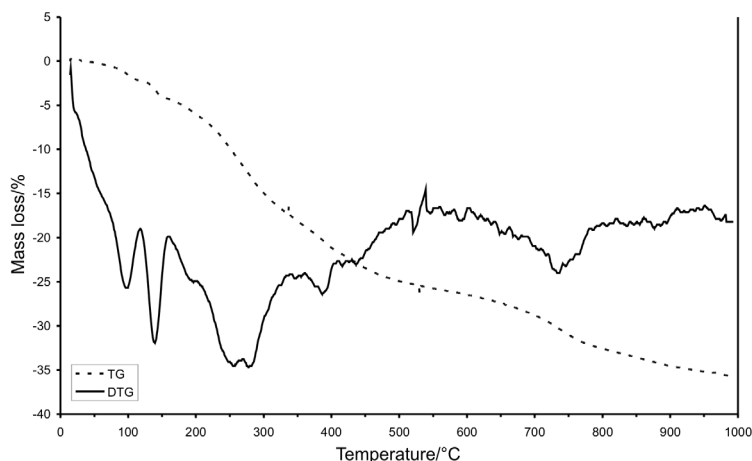


Fig. 5 TG curve of the investigation of SRM 1649a in nitrogen, heating rate 10 K min^{-1}

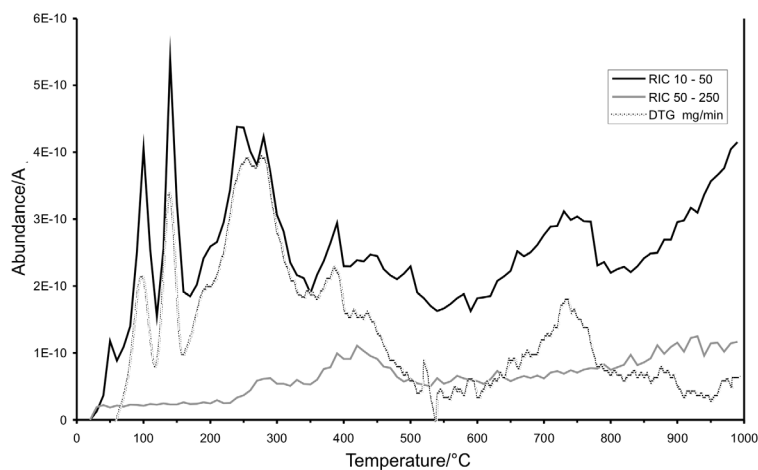


Fig. 6 Ion current intensities vs. temperature of the investigation of SRM 1649a

The mass spectrum at 290°C , the main peak of the low mass region (Fig. 7) shows besides the evolution of water (m/z 16, 17 and 18) fragments at m/z 44, 48 and 64. This is due to the evolution of SO_2 (m/z 64, 48) and CO_2 (m/z 44). The temperature dependence of these ion current intensities is given in Fig. 8. From this figure, the weakly and strongly bonded moisture as well as different crystal waters can be observed from the m/z 18 curve. Further, the degradation of different carbonates (m/z 44) and sulphates (m/z 64, 48) can be observed.

From the mass spectral overview in Fig. 9, there are also some fragments in the higher mass region. In the temperature range from about 250 to 500°C , ions in the region m/z 80–130 occurred. They are due to toluene and other side chain alkylated

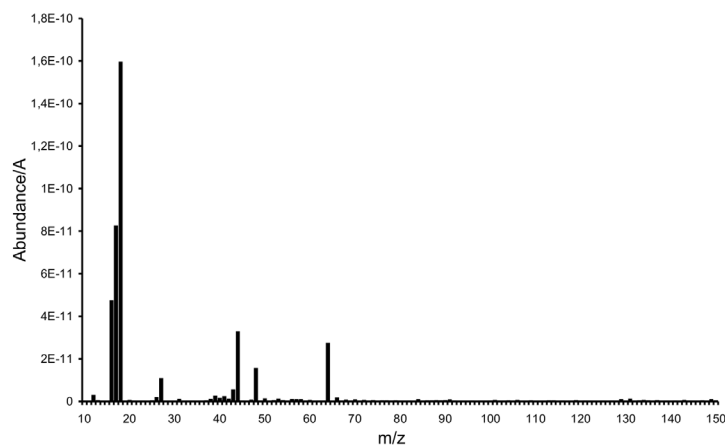


Fig. 7 Mass spectrum of the investigation of SRM 1649a at 290°C

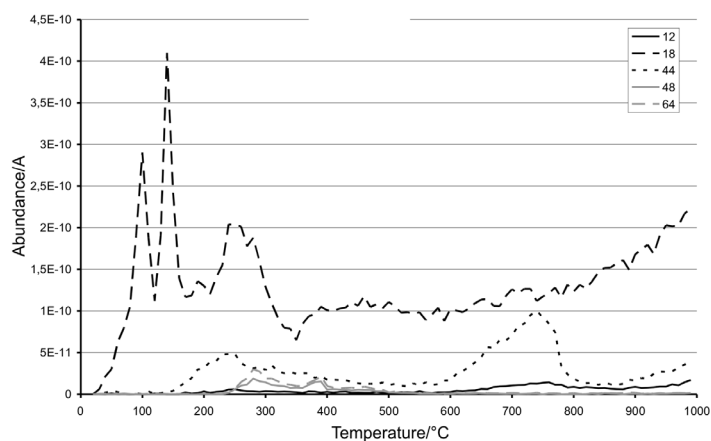


Fig. 8 Ion current intensities vs. temperature of the investigation of SRM 1649a

benzenes (m/z 91), phenols (m/z 94) and condensed aromatics (naphthalene m/z 128). Further high mass fragments were not detected.

Thermal analysis GC-MS

Since TA-MS investigations have revealed the occurrence of organic compounds for all samples, an identification of the individual components is of great interest. Due to the limited sensitivity and the fact, that no separation of the mixed gases is possible, additional GS-MS investigations were carried out. During these experiments, the samples were heated from room temperature to 850°C (10 K min⁻¹) in helium atmosphere and the evolved gases were introduced directly into a GC-column. During the whole heating step, the evolved gases were trapped directly on the analytical column

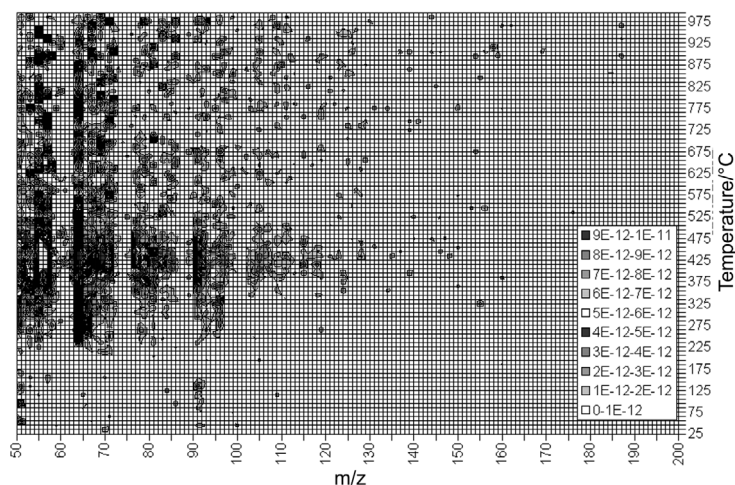


Fig. 9 Mass spectral overview of the investigation of SRM 1649a

using a micro jet cryo-trap with liquid nitrogen. After this 'desorption step', the components were separated on the GC-column and detected by MS.

From the CAST samples, only CAST 273 was investigated using TA-GC-MS since TA-MS investigations did not allow the assignment of individual components. The chromatogram of this investigation shows a huge number of different compounds being evolved during the heating process (Fig. 10).

Besides some inorganic compounds like CO_2 , SO_2 , ammonia and water a large number of different organic compounds could be detected. In Table 2 some of the identified compounds are listed. The identification was done by an automated comparison of the measured mass spectra with standard library spectra (NIST). The table was created of those substances which showed during the automated search procedure a match quality greater than 85%.

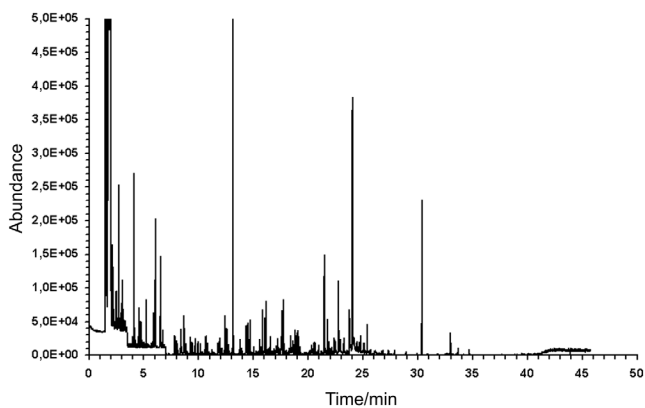


Fig. 10 TD-GC/MS chromatogram of CAST 273

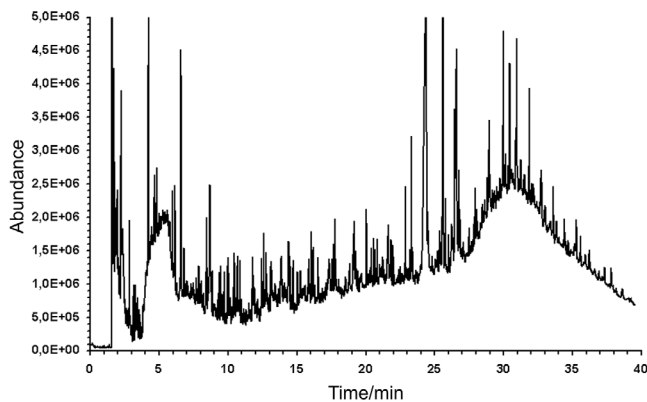
Table 2 Identified compounds from CAST 273, match quality >85%

t_R	Library/ID	t_R	Library/ID
1.52	Carbon dioxide	11.87	1H-Indene, 1-methyl-
1.57	Sulphur dioxide	11.92	Benzene, pentyl-
1.62	1-Propene, 2-methyl-	12.41	Naphthalene
1.67	Ammonia	12.57	1-Dodecene
1.72	Water	12.74	Dodecane
1.83	1,3-Butadiene, 2-methyl-	13.13	Benzothiazole
2.16	1-Hexene	13.91	1H-Indene, 1,1-dimethyl-
2.22	Hexane	13.98	Naphthalene, 1,2-dihydro-6-methyl-
2.25	Furan, 2-methyl-	14.36	1-Tridecene
2.64	1,3-Pentadiene, 3-methyl-, (E)-	14.41	Naphthalene, 2-methyl-
2.72	Benzene	14.51	Tridecane
2.92	Bicyclo[3.1.0]hexane	14.7	Naphthalene, 1-methyl-
3.03	1-Heptene	15.57	Benzene, heptyl-
3.15	Heptane	15.83	Naphthalene, 2-ethenyl-
3.29	2-Hexene, 5,5-dimethyl-, (Z)-	16.04	1-Tetradecene
3.35	2-Heptene, (E)-	16.17	1,1'-Biphenyl, 2-methyl-
4.13	Toluene	16.51	Naphthalene, 2,6-dimethyl-
4.54	Heptane, 3-methylene-	16.7	Benzene, 1,1'-methylenebis-
4.57	1-Octene	16.88	Naphthalene, 2,6-dimethyl-
4.86	3-Octene, (E)-	17.09	1H-Isoindole-1,3(2H)-dione
5.02	Cyclooctane	17.54	1,1'-Biphenyl, 4-methyl-
5.91	Ethylbenzene	17.62	1-Pentadecene
6.07	p-Xylene	17.75	Pentadecane
6.5	Styrene	18.26	Naphthalene, 2,3,6-trimethyl-
6.56	Benzene, 1,2-dimethyl-	18.41	1,6-Dioxacyclododecane-7,12-dione
6.75	Nonane	19.04	Fluorene
6.87	Cyclopropane, 1-methyl-2-pentyl-	19.24	Hexadecane
7.89	Benzene, isocyanato-	20.66	Heptadecane
8.33	Aniline	21.48	Tetradecanoic acid
8.38	Benzene, 1,2,3-trimethyl-	21.76	Benzenesulfonamide, N-butyl-
8.46	Phenol	21.92	11-Tricosene
8.84	Decane	22.01	Pentadecane
9.26	Benzene, 1,2,3-trimethyl-	22.77	Pentadecanoic acid
9.32	Benzene, 2-propenyl-	23.82	9-Hexadecenoic acid
9.41	Limonene	24.44	1-Docosene

Table 2 Continued

t_R	Library/ID	t_R	Library/ID
9.69	Benzene, 1-propynyl-	24.52	Heneicosane
9.95	Benzene, (2-methylpropyl)-	24.79	Hexadecanoic acid
10.16	Benzene, 1-methyl-2-propyl-	26.81	Pentadecane
10.68	1-Nonene	27.89	Heptadecane
10.84	Hexadecane	30.38	Bis(2-ethylhexyl) phthalate
11.25	Benzene, 1-ethenyl-4-ethyl-		

The chromatogram of the investigation of urban dust (SRM 1649a) is given in Fig. 11. In comparison to the CAST sample, it shows much more individual compounds overlaying each other. A first evaluation based on the deconvolution of the mass spectral data using the NIST AMDIS (Automated Mass Spectral Deconvolution & Identification System) program revealed about 1600 individual compounds. An identification of individual compounds was done using a target library with 250 components. The results of this first assignment are listed in Table 3.

**Fig. 11** TD-GC/MS chromatogram from SRM 1649a**Table 3** Identified compounds from SRM 1649a (Urban Dust), match quality >85%

Library/ID	Library/ID
1,1':3',1":3",1'''-Quaterphenyl	Cyclooctane
1,3-Butadiene, 2-methyl-	Cyclopropane, 1-methyl-2-pentyl-
1,3-Pentadiene, 3-methyl-, (E)-	Cyclotetradecane
1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	Dibutyl phthalate
1,8-Naphthalic anhydride	Ethylbenzene
1-Heptene	Furan, 2-methyl-
1-Hexanol, 2-ethyl-	Heneicosane

Table 3 Continued

Library/ID	Library/ID
1-Hexene	Heptadecane
1H-Indene	Heptane
1H-Isoindole-1,3(2H)-dione	Heptane, 3-methylene-
1-Octene	Heptanoic acid
1-Propene, 2-methyl-	Hexadecanenitrile
1-Tridecene	Hexane
2,6-Dichloroxanthen-9-one	Lauric anhydride
2-Heptene, (E)-	Naphthalene
2-Hexene, 5,5-dimethyl-, (Z)-	Naphthalene, 2-phenyl-
3-Octene, (E)-	<i>n</i> -Decanoic acid
8,9-Dihydrocyclopenta[def]phenanthrene	<i>n</i> -Hexadecanoic acid
9,10-Anthracenedione	Nonane
9H-Fluoren-9-one	Octacosane
9H-Fluorene, 9-methylene-	Octadecanoic acid
Acetophenone	Octanoic acid
Ammonia	Pentacosane
Aniline	Pentadecanoic acid
Anthracene, 1-methyl-	Perylene
Benz[a]anthracene	Phenanthrene
Benz[b]fluoranthene	Phenol
Benzene	Phenol, 4-methyl-
Benzene, (2-methylbutyl)-	Picolinamide
Benzene, (2-methylpropyl)-	<i>p</i> -Xylene
Benzene, 1,1'-(1,3-propanediyl)bis-	Pyrene
Benzene, 1,2,3-trimethyl-	Quinoline
Benzene, 1,2-dimethyl-	Quinoline, 2,4-dimethyl-
Benzene, isocyanato-	Squalene
Benzo[ghi]fluoranthene	Styrene
Benzo[j]fluoranthene	Sulphur dioxide
Benzo[k]fluoranthene	Tetracosane
Benzofuran, 2,3-dihydro-	Tetradecanoic acid
Benzoic acid	Toluene
Bicyclo[3.1.0]hexane	Tridecane
Biphenyl	Undecane
Bis(2-ethylhexyl) phthalate	Water
Carbon dioxide	

Conclusions

From these investigations, several conclusions can be drawn.

- The CAST system is not able to produce carbonaceous particles that are free of organic load. So artificial aerosol particles from CAST systems cannot be used to test the influence of the particle itself.
- The used coupled thermoanalytical instrument is currently not sensitive enough to identify organic compounds on aerosol particles. Additional investigations are necessary.
- Further instrumental developments may overcome the limitations of the direct coupled thermal analysis / mass spectrometry device.
- Complex samples need several complementary methods of investigation. A combination of thermal methods with others will bring a deeper understanding of the sample.

* * *

The authors like to thank the ESI Enviro Service International GmbH, Munich for the supply of the Frontier Lab Double Shot Pyrolysis GC/MS system.

References

- 1 S. M. Dakka, *J. Therm. Anal. Cal.*, 74 (2003) 729.
- 2 D. F. Parra, L. P. Mercuri, J. R. Matos, H. F. Brito and R. R. Romano, *Thermochim. Acta*, 386 (2002) 143.
- 3 N. Hurduc, A. Creanga, G. Pokol, Cs. Novák, D. Scufaru, S. Alazaoarie and H. Hurduc, *J. Therm. Anal. Cal.*, 70 (2002) 877.
- 4 B. Ptaszynski and A. Zwolińska, *J. Therm. Anal. Cal.*, 75 (2004) 301.
- 5 D. Czakis-Sulikowska and A. Czyrkowska, *J. Therm. Anal. Cal.*, 74 (2003) 349.
- 6 B. Ptaszynski and Zwolińska, *J. Therm. Anal. Cal.*, 74 (2003) 237.
- 7 D. Czakis-Sulikowska, A. Czyrkowska and A. Malinowska, *J. Therm. Anal. Cal.*, 67 (2003) 667.
- 8 G. G. Mohamed, Nour El-Dien, F. A. El-Gamel and E. A. Nadia, *J. Therm. Anal. Cal.*, 67 (2002) 135.
- 9 J. Douda, M.-E. Llanos, R. Alvarez, C. López Franco and J.-A. Montoya de la Fuente, *J. Anal. Appl. Pyrol.*, 71 (2004) 601.
- 10 V. Strezov, J.-A. Lucas and L. Strezov, *J. Anal. Appl. Pyrol.*, 71 (2004) 375.
- 11 X. Li, G. Matuschek, M. Herrera, H. Wang and A. Kettrup, *J. Anal. Appl. Pyrol.*, 67 (2003) 393.
- 12 X. Li, G. Matuschek, M. Herrera, H. Wang and A. Kettrup, *J. Therm. Anal. Cal.*, 71 (2003) 601.
- 13 P. Pagano, T. De Zaiacomo, E. Scarcella, S. Bruni and M. Calamosca, *Environ. Sci. Technol.*, 30 (1996) 3512.
- 14 D. W. Dockery, C. A. Pope II, X. Xu, J. D. Sprenghler, J. H. Ware, E. F. Martha, B. G. Ferris Jr. and F. E. Speizer, *New Engl. J. Med.*, 329 (1993) 1753.
- 15 J. Schnelle-Kreis, I. Gebefugi, G. Welzl, T. Jaensch and A. Kettrup, *Atmos. Environ.*, 35 (2001) S71.
- 16 J. Schwartz, D. W. Dockery and L. M. Neas, *J. Air Waste Manage. Assoc.*, 46 (1996) 927.