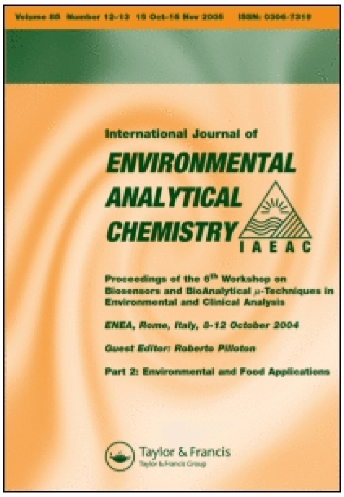

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Puxbaum, Hans(1981) 'Application of Two Thermo-gas-analyzers for Atmospheric Aerosol Characterization', International Journal of Environmental Analytical Chemistry, 10: 1, 1 — 6
To link to this Article: DOI: 10.1080/03067318108071525
URL: http://dx.doi.org/10.1080/03067318108071525

Intern. J. Environ. Anal. Chem., 1981, Vol. 10 pp. 1–6
0306-7319/81/1001-0001 $06.50/0

Printed in Great Britain

Application of Two Thermo-gas-analyzers for Atmospheric Aerosol Characterization†

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(*Received May 30, 1980*)

Two thermo-gas-analyzers were applied for characterization of carbonaceous and sulphurous compounds in atmospheric aerosol samples. Sampling of the atmospheric aerosol is carried out with a four stage low pressure cascade impactor, type "Berner TU 80" with a deposition range of 0.1–25 μm AD.

Thermo-gas-analysis of the sized samples is carried out in nitrogen atmosphere and detection of volatile organic compounds "VOC" by FID. Thermo-gas-analysis in oxygen atmosphere with detection of evolved CO_2 and SO_2 separates the fractions "organic carbon", "organic debris", "soot carbon", "carbonate carbon", "converted sulphur", "soot sulphur" and "thermally stable sulphur". Enrichment of "VOC", "organic carbon", "soot carbon" and "converted sulphur" takes place in the "accumulation mode" whereas "organic debris", "carbonate carbon" and "thermally stable sulphur" are found predominantly in the "coarse particle mode".

KEY WORDS: Atmospheric aerosol, carbon and sulphur analysis, size distribution of aerosol components

INTRODUCTION

The chemical composition of atmospheric aerosols varies with time and space. Within these variations dynamic changes of the size distribution of the aerosol components occur. Speciation of chemical components as a function of particle size is carried out by size fractionated sampling with cascade impactors and analysis of the fractions with "thermo-gas-analytical-methods". With two "thermo-gas-analyzers" the fraction "volatile organic carbon", "organic carbon", "organic debris", "soot",

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†Presented at 10th Annual Symposium on the Analytical Chemistry of Pollutants, May 28–30, 1980 Dortmund.

"carbonate carbon", "converted sulphur", "soot sulphur" and "thermally stable sulphur" are separated.

Aerosol balances of groups of compounds with different thermal behaviour include the main components of the atmospheric aerosol.[2]

APPARATUS

Temperature programmed treatment of the aerosol sample is carried out in atmospheres of nitrogen and oxygen (Figure 1).

1. "VOC"—Volatile organic carbon

Volatile organic carbonaceous components are detected by a flame-ionization-detector during temperature programmed desorption (TPD-FID). The apparatus is calibrated with a mixture of organic compounds representative for substances frequently occurring in the atmosphere (hydrocarbons, PAH, organic acids). The method was tested in the working range 0.1–50 μg "VOC", sample weights were 50–500 μg.

2. "TDCS"—Temperature differentiated carbon- and sulphur analysis

Temperature programmed treatment of aerosol samples in oxygen atmosphere allows separation of four fractions of carbonaceous compounds and three fractions of sulphurous compounds.

The "TDCS"-apparatus (Figure 1) is a combined system of a temperature programmed furnace and continuously recording relative conductimetric SO_2 and CO_2 detectors. Sensitivity of the detectors is 40 ng $S\,s^{-1}$ and 400 ng $C\,s^{-1}$ recorder full scale (200 mm), sample weights are 50–200 μg.

3. Aerosol sampling

Atmospheric aerosol samples were collected with high performance low pressure impactors, designed by A. Berner.[3] The aerosol is separated into four size fractions logarithmically divided in the range 0.1–25 μm AD. Using a sampling rate of 80 l min^{-1} sampling intervals of four hours provide sufficient material for aerosol characterization.[4]

RESULTS

1. Modality of aerosol components

Despite of the low resolution of the four stage impactor urban aerosols

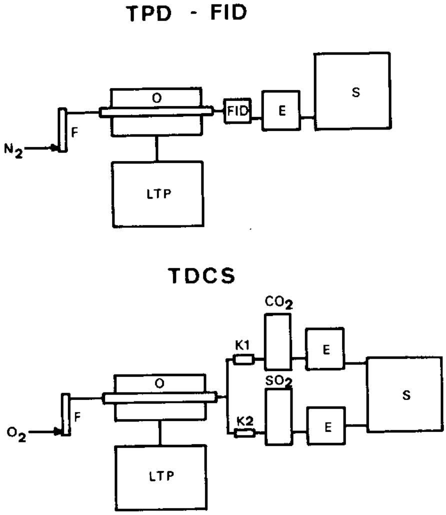

FIGURE 1 Temperature programmed decomposition of atmospheric aerosol samples. TPD-FID: Nitrogen-atmosphere, TDCS: Oxygen-atmosphere O furnace, LTP linear temperature programmer, F flowmeter, E electronics, S recorder, K 1 scrubber (Ag 500°C), K 2 scrubber ($AgSO_4$-$KHSO_4$), CO_2, SO_2 gas analyzers.

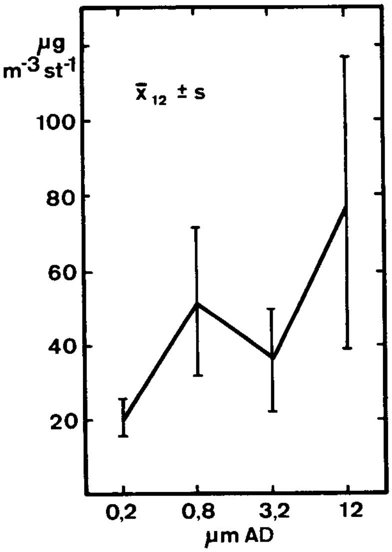

FIGURE 2 Mass-size distribution. Atmospheric aerosol samples Vienna, Getreidemarkt, Mean values of 12 samples, December 1976, sampling time 12 hours. st = impactor stage.

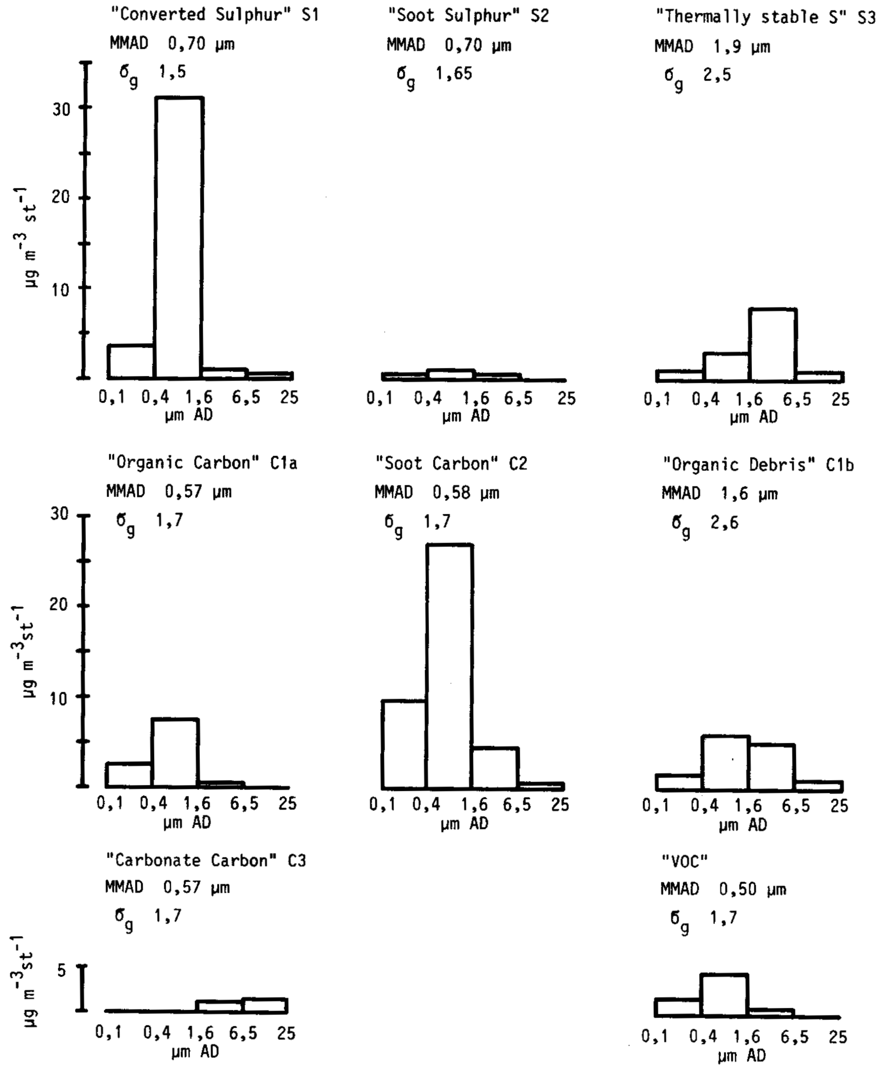

FIGURE 3 Size distribution and modal parameters of aerosol components, Aerosol sample G 3 Getreidemarkt Vienna Oct. 1978 (S 1 values expressed as $(NH_4)_2SO_4$, S 3 as $CaSO_4$).

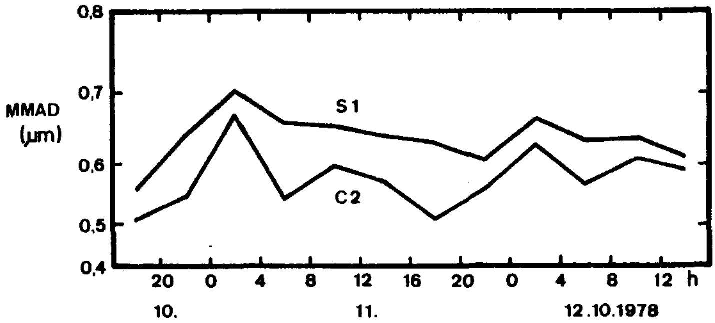

FIGURE 4 Temporal change of MMAD's of "converted sulphur" (S 1) and "soot carbon" (C 2) in aerosol samples collected in Vienna, Getreidemarkt. Location heavily influenced by traffic.

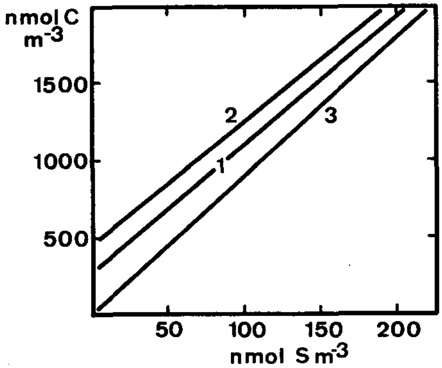

FIGURE 5 Linear regression: "converted sulphur"—"soot carbon"

Curve	Fraction	Size (μm)	k	d	r
1	S_{CONV}-C_{TOTAL}	0.1–0.4	8.4	276	0.67
2	S_{CONV}-C_{TOTAL}	0.4–1.6	8.1	445	0.57
3	S_{CONV}-$C_{SOOT/AGED}$	0.1–1.6	8.7	−7	0.94

k = slope, d = intercept, r = lin. coefficient of correlation, $n = 12$ values.

show a distinct bimodality of the mass-size distribution in the size range observed (Figure 2).

Application of thermo-gas-analytical techniques for analysis of the impactor collected samples showed the distinct enrichment of carbon- and sulphur-species in different regions within the size-range of 0.1–25 μm AD. The modal parameters of the analyzed species were evaluated by graphical interpolation of log-probability plotted size distributions. Log-normal distributions of the different modes was assumed according to the results of K.T. Whitby.[5] Furthermore no bimodality within a species was detected by analyzing cumulative frequency plots in the linear scale.

Results of the modal evaluation reveal deviations of the "ideal bimodality" (Figure 3). Mass median aerodynamic equivalent diameters (MMAD's) of the organic carbon, soot carbon and volatile organic carbon fractions are shifted towards smaller diameters compared to the conversion sulphate fraction. This shift is explained by the influence of emissions of mobile sources at the sampling location. The "organic debris" mode is situated "between" the "accumulation" and the "coarse" mode. "Carbonate carbon" and "thermally stable sulphates" are part of the coarse mode but also showing different modal parameters indicating non-uniformity of the "coarse mode".

2. Time series

Temporal changes of aerosol composition was monitored for two days with the sampling intervals of four hours. Evaluation of modal parameters of the fractions dominating the "accumulation mode" shows a shift of the "soot carbon mode" towards smaller values as compared to the "converted sulphur mode" (Figure 4). Correlation of "converted sulphur" and "total carbon" concentrations in the two smaller size fractions was not good (Figure 5). Correlating "converted sulphur" with "soot-carbon aged" an excellent coefficient of correlation was obtained. "Soot carbon aged" is the "soot carbon fraction" minus the fraction of "soot carbon" which is produced by vehicles in the vicinity of the sampling location. The correction procedure has been described already.[1] The "soot carbon" produced by vehicles was calculated from vertical profile measurements.

Acknowledgements

Initiation of this work by Professor Malissa is appreciated.

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