

Identification of homologous series as organic tracers in PM samples: a signal processing method for studying complex GC-MS signals

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Homologous series of n-alkanes and n-alkanoic acids are especially suited as molecular markers to give information relevant to trace the origin and fate of atmospheric aerosols. Two main parameters are used as chemical signature to differentiate anthropogenic vs. biogenic sources: the number of terms of the series (n_{max}) and the carbon preference index (CPI) which represents the prevalence of odd/even carbon number terms of the series.

Gas chromatography-mass spectrometry (GC-MS), the best analytical technique for these organics, generates extensive amounts of data when applied to such complex mixtures as polluted environmental samples, which are complicated by a vast amount of noise, artefacts, and data redundancy.

In the present paper, a signal processing procedure based on the AutoCovariance Function ($ACVF_{tot}$) is applied to GC-MS signals of atmospheric aerosols. This is a computer-assisted signal processing procedure able to transform GC data into usable information by extracting all the analytical results hidden in the complex chromatogram (Pietrogrande *et al.*, 2007). The method is further extended by deriving new mathematical equations and implementing a new computation algorithm to extract information on the homologous series -- n_{max} and CPI -- directly from the experimental $EACVF_{tot}$ computed on the acquired chromatographic signal (Pietrogrande *et al.*, 2008, Pietrogrande *et al.*, 2009).

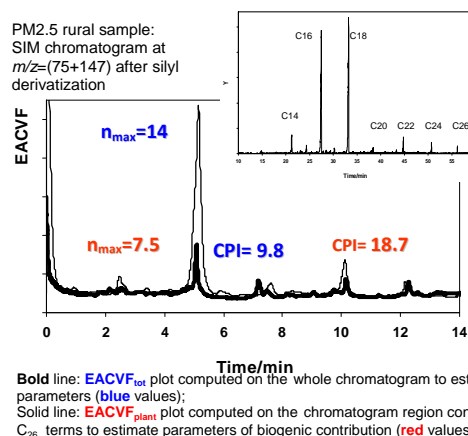
The procedure was validated on simulated chromatograms with known distribution of the terms of the series: the obtained results prove that the parameters n_{max} and CPI of the homologous series can be estimated with good accuracy and precision.

The method was applied to experimental chromatograms of real samples: aerosol samples ($PM_{2.5}$ and PM_{10}) were collected daily in urban and rural sites. The information on distribution pattern of n-alkanes and n-alkanoic can be directly obtained from the $EACVF_{tot}$ computed on the acquired chromatogram, thus reducing the labour and data handling time and removing the subjective step of peak integration. The advantages of the method can be singled out by comparison with the traditional procedure based on GC peak identification and integration.

The procedure was used to investigate the distribution profile of n-alkane (C_{14} – C_{33} terms) and n-alkanoic acid (C_{14} – C_{26} terms) homologous series. The

number of terms and CPI_{tot} values were computed directly from the $EACVF_{tot}$ from the whole chromatogram. Moreover, the procedure can be separately applied to the chromatographic region containing the biogenic heavier terms of the series to compute the $EACVF_{plant}$: the obtained parameters n_{plant} and CPI_{plant} give quantitative information on the role played by the biogenic vs. anthropogenic sources.

The series of n-alkanoic acids was investigated as useful marker in discriminating sources contribution to the aerosol organics: high CPI_{tot} values, confirming the even prevalence of acid isomers mostly derived from plant waxes, were found for rural and urban samples. Information on the biological sources of n-alkanoic acids can be simply extracted by computing $ACVF_{plant}$ on the selected chromatographic region containing the C_{20} – C_{26} terms: the estimated CPI_{plant} reflects the vascular plant wax signature. A simple graphical comparison of $EACVF_{plant}$ with $EACVF_{tot}$ gives quantitative information on the contribution of the biological sources of atmospheric n-alkanoic acids.



The described signal processing method seems promising for high-throughput analysis of the large data sets generated by chemical monitoring in environmental analysis.

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