Determination of low-molecular-weight dicarboxylic acids in atmospheric aerosols: comparison between silylation and esterification derivatisation procedures for GC-MS analysis

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Aliphatic dicarboxylic acids are one of most important components of water-soluble organics in atmospheric aerosol: they can derive from primary emissions from biomass burning and fossil fuel combustion, as well as photochemical oxidation of organic precursors of both anthropogenic and biogenic origin. Therefore, a detailed investigation on concentrations and relative abundance of these compounds can help us to evaluate the importance of secondary photochemical reactions.

In particular low-molecular-weight (LMW) dicarboxylic acids (C3-C10) gives important chemical information for source apportioning of aerosol organics and for studying atmospheric processes leading to secondary organic aerosol formation: the C3/C4 ratio has been suggested as indicator of enhanced photochemical production of dicarboxylic acids in the atmosphere and the C6/C9 ratio may be assumed as a potential indicator of source strength of anthropogenic and biogenic precursors to the aerosol diacids (Kawamura et al., 2005).

To date, GC-MS is the method of choice for characterizing individual organic compounds within aerosol samples, primarily because shows sensitivity, precision and accuracy required in environmental studies. The high polarity and low levels of carboxylic acids pose special challenges for their identification and quantification because require preliminary chemical derivatisation, i.e., conversion to less polar compounds to be eluted through a GC column.

Two derivatisation processes using different reagents and catalysts have been developed and widely used over the years for dicarboxylic acid determination in PM samples (Manish et al., 2007): 1) esterification of the acid groups using methanol or 1-butanol as derivatising agents in the presence of a Lewis acids (often BF3) as catalyst:

\[
\text{RCOO} + \text{R'OH} \rightleftharpoons \text{RCOOR'} + \text{BF}_3
\]

2) silylation based on a silylation reagent that introduces –Si(CH3)3 groups in the molecules, (Figure 2), i.e., N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS), were investigated.

This paper is focused on the determination of LMW dicarboxylic acids (C3-C10): the most widely used procedures, i.e., esterification with butyl alcohol and BF3 like catalyst and a silylation with N,O-bis-(Trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS), were investigated. For each method, the effect of various experimental parameters on the reaction yield has been investigated and optimized: time and temperature, or amount of reagents. The better procedure was searched for the faster one-step derivatisation to determine C3-C10 dicarboxylic acids as target compounds.

The advantages and drawbacks of the methods are investigated and compared in terms of precision and accuracy of the obtained results, sensitivity and detection limit of the procedure.

The obtained results show that the silylation procedure is the method more compatible with application to chemical analysis in PM samples: satisfactory precision and accuracy are obtained for all the studied acids at the sub-nmol level at which the dicarboxylic acids are expected to be present in trace levels (Manish et al., 2007). Butyl esters of low molecular weight dicarboxylic acids are too volatile to yield evaporative losses and too unstable to be accurately quantified so that quantification was possible for the C4-C9 dicarboxylic acids.

The precision and accuracy were investigated by comparing results obtained by the two procedures from the simultaneous analysis of dicarboxylic acids in the same PM2.5 and PM10 samples.