CAPILLARY ELECTROPHORESIS DETERMINATIVE and GC-MS CONFIRMATORY METHOD for WATER-SOLUBLE ORGANIC ACIDS IN AIRBORNE PARTICULATE MATTER and VEHICULAR EMISSION

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AIM of the STUDY

- The accurate and efficient determination of LMW organic acids in both ambient air samples and emission samples is crucial to the understanding of many aspects of air quality and health-related issues.
- CE procedure with indirect UV detection was successfully implemented in the routinely analysis of a variety of water-soluble organic acids in urban atmospheric aerosols and vehicle emissions.
- The key advantage of CE derives from its greater efficiency and resolution, speed, simplicity, and economy compared to more conventional chromatographic techniques.
- However, CE with indirect UV detection lacks the analytical specificity for individual organic acids, which sometimes results in identification and quantification difficulties.
- This work focused on confirmation and/or identification of water-soluble organic acids in urban fine PM and in vehicular emissions using GC-MS.

Background & Motivation

- Atmospheric fine particulate matter (PM) plays a key role on climate issues and health problems.
- PM consists of a complex mixture of inorganic as well as carbonaceous compounds that are directly emitted from sources and material that condenses as a product of gas-phase chemical reactions.
- Carbonaceous species, organic carbon (OC) and elemental carbon (EC), constitute a major, sometimes dominant, fraction of PM.
- OC represents a large variety of organic compounds.
- Less information is available on the water-soluble LMW carboxylic acids found in the urban atmospheric fine PM and vehicular emissions.
- Given the potential importance of carboxylic acids, their accurate and efficient quantification is crucial to the understanding of many aspects of particle chemistry.

EXPERIMENTAL

- Urban and vehicle emitted PM were collected on Teflon filters were extracted with 8 ml of D.I. water in an ultrasonic bath for 30 min.
- Gas-phase vehicle exhaust samples collected on KOH-coated quartz fibre filters were extracted with 10 ml of D.I. in an ultrasonic bath for 30 min.
- In the confirmatory (this) study, bulk solutions were prepared from frozen residues of extracts previously analyzed by CE and IC.
- The bulk solutions were analyzed by both CE and GC-MS methods.

**CE**

- Sample preparation & analysis

**GC-MS**

- Sample preparation & analysis

RESULTS & DISCUSSION

- Low C3 monocarboxylic acids (formic, acetic and propionic) not observed by GC-MS due to loss during evaporation stages
- Confirmation of dicarboxylic acids from C2 to C10, including glyceric, lactic, malic and maleic.
- Confirmation of aromatics such as benzene, p-toluic, isophthalic, tert-phthalic and methylphthalic.

SUMMARY

- GC-MS was used to definitely identify a variety of water-soluble organic acids in airborne fine PM and vehicle emitted samples.
- These results confirm the presence of acids previously determined by CE with indirect UV detection and are in agreement with the literature.
- CE separates major mono- and dicarboxylic acids, but the minor ones are either unresolved or not detected due to their low concentrations.
- GC-MS is the more selective technique for the aromatic and oxocarboxylic acids separation, and therefore preferred whenever quantification of such acids is required.
- CE analyses are significantly faster and cheaper. Therefore, if attention is focused on the major organic acids, CE is a quite valuable analytical technique.
- As expected, MS in combination with GC proved to be a useful tool for solving varied types of analytical problems (e.g. peak purity), confirmed structure identity and provided mass spectral information.
- However, unlike analysis by CE, GC-MS is a time-consuming multi-step procedure, which requires a derivatization step and could incorporate artifacts in the sample, as evidenced by the baseline in the chromatograms.