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.

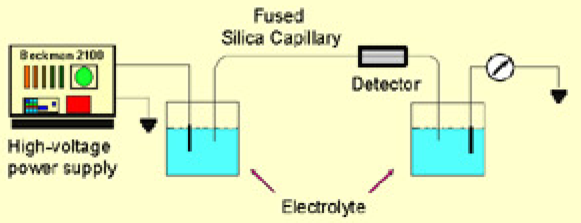
Background & Motivation

- 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 emission.
- Given the potential importance of carboxylic acids, their accurate and efficient quantitation 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



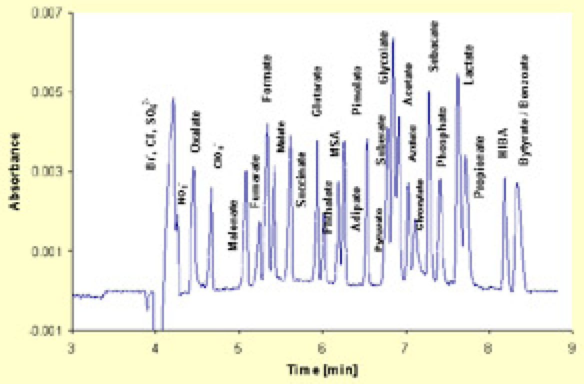


Figure 1
E. Dabek-Zlotorzynska et al. J. Chromatogr. A, 910 (2) (2001) 331-345.

- **BGE:** 4 mM NDC - 0.2 mM TTAB, pH 6.2 (14.4 mM Bis-Tris)
- **Capillary:** 75 µm I.D. x 57 cm (50 cm to detector)
- **Detection:** Indirect UV, 214 nm
- **Control Mode:** Constant current (6.6 ± 0.6 µA)
- **Temperature:** 25 °C
- **Injection:** Pressure 10 s; 2s BGE; Electrokinetic (EK) 10 kV, 15 s

GC-MS

sample preparation & analysis

10 mL Bulk sample
Evaporated to dryness with N2
DERIVATIZATION 0.7 mL BF3/Butanol
EXTRACTION with hexane
Evaporation
GC-MS analysis

- **GC-MS analysis**
  - GC/MS HP 6890 series
  - DBXLB capillary (0.25 mm i.d. x 30 m x 0.25 mm), temp program 50°C for 2 min and then to 300°C at 8°C/min
  - Mass selective detector HP 5973, scan mode (range m/z 50-500)
- **Confirmatory MS and RT with standards**
  - At least 80% match with Nist98 library
  - In case of Cw acids, fragmentation reported by Kawamura *et al.* (1993)

Key Organic Acids

in Ambient Air & Motor Exhaust Samples

- **Monocarboxylic acids (30% total acidity)**
  - formic (C1), acetic (C2)
- **Dicarboxylic acids (C2-C4: ~80%)**
  - oxalic (C_2^{di}), malonic (C_3^{di}), succinic (C_4^{di}), fumaric (hC_4^{di}), glutaric (C_5^{di}), adipic (C_6^{di}), pimelic (C_7^{di}), suberic (C_8^{di}), azelaic (C_9^{di}), sebacic (C_{10}^{di})
- **Hydroxycarboxylic acids**
  - glycolic (hC_2), lactic (hC_3), malic (hC_4)
- **Ketoacids**
  - pyruvic (Pyr), glyoxylic (Gly); ketomalonic
- **Aromatic acids**
  - benzoic (benz), phthalic (Ph); isophthalic (i-ph); terephthalic (t-ph); metaphthalic (m-ph); methylphthalic

RESULTS & DISCUSSION

- Low C_n monocarboxylic acids (formic, acetic and propionic) not observed by GC-MS due to loss during evaporation stages
- Confirmation of dicarboxylic acids from C_2 to $C_{9\text{-}10}$ including glycolic, lactic, malic and maleic
- Confirmation of aromatics such as benzoic, phthalic, isophthalic, terephthalic and methylphthalic.

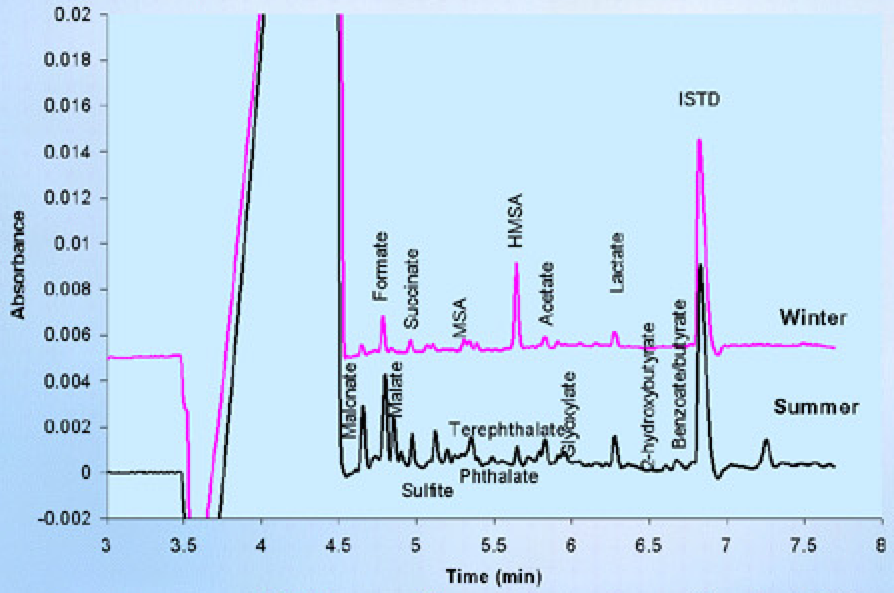


Fig. 2. CE Example of Toronto collected PM

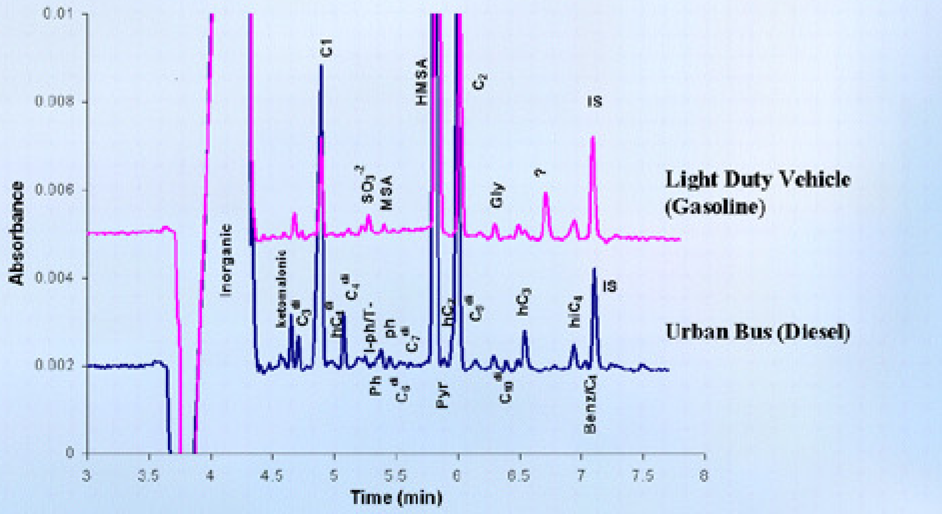


Fig. 4. CE Example of Vehicle Emission Sample

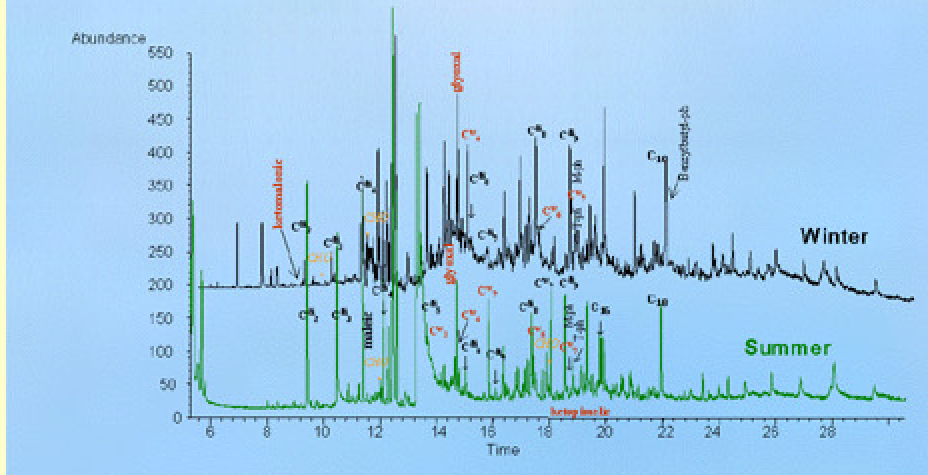


Fig. 3. GC-MS Example of Toronto collected PM

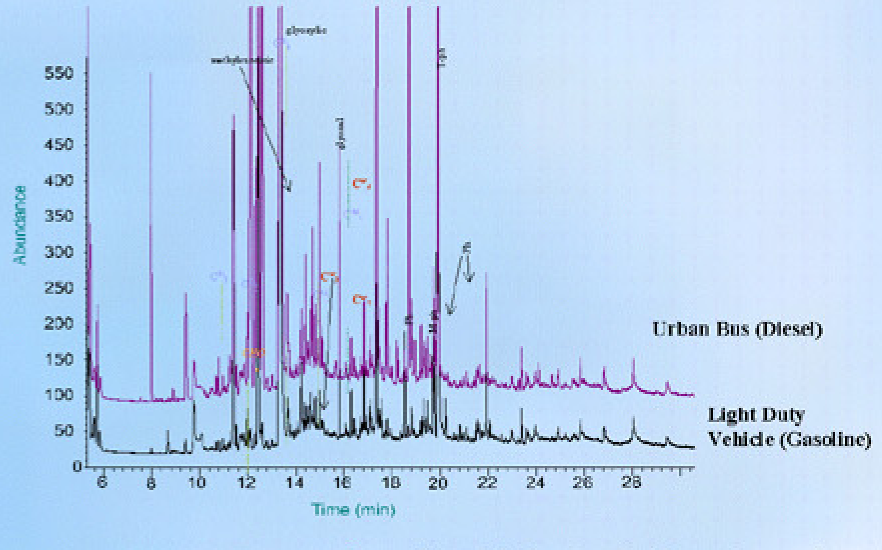


Fig. 5. GC-MS Example of Vehicle Emission Sample

SUMMARY

- GC-MS was used to definitely identify a various 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.