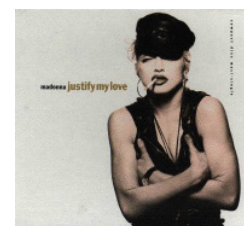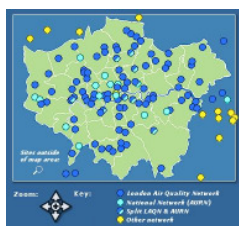# Determination of Organic Acids in Airborne Particulate Matter
Collected in Marylebone Road, London
by Two-Dimensional Capillary Isotachophoresis

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London street scene, the continuous monitoring sites of the London Air Quality Network (http://www.londonair.org.uk), the Marylebone Road / Baker Street sampling site, "PM10 Particulate" filters from different days -- and one of Marylebone's better known residents.

Introduction / Background

Airborne particulate matter (APM) has diverse origins customarily divided into primary sources such as vehicular exhausts and secondary sources which involve chemical reactions in the atmosphere. It is thought to play an important role in atmospheric chemistry and also to be hazardous to health. Because APM consists of a wide range of inorganic and organic components, its chemical characterisation presents a significant analytical challenge, particularly with respect to polar organic molecules.

Mono- and dicarboxylic acids are known to be present in APM and have been measured by gas chromatography (GC), liquid chromatography (HPLC), and ion chromatography (IC); however, these methods suffer with either tedious sample preparation (e.g. derivatization in GC) or potentially insufficient separation efficiency / selectivity (HPLC, IC). Additionally, the concentration of the low molecular-weight acids extracted from the sampling filters is generally in the middle to lower μg/l-range, and the concentration of the higher diacids is close to the detection limits of existing capillary zone electrophoresis (CZE) and IC methods. Therefore, an analytical method with higher sensitivity (and preferably minimal sample preparation) would be very useful.

Objectives

We are currently investigating the possibility of coupling isotachophoresis (ITP) with CZE to pre-concentrate the analytes, and to remove excess inorganic ions (e.g., sulfate, nitrate, chloride), the concentrations of which are one to two orders of magnitude higher than those of the organic acids.

This poster presents the development of the ITP methodology (still in progress) and preliminary results for APM samples collected in central London.

Options to improve the sensitivity and selectivity of the ITP step, and to simultaneously determine inorganic and organic ions are briefly outlined. Ultimately, the aim is to combine online ITP-CZE with MS detection.

**Method Development with 9 Acids as Model Analytes**
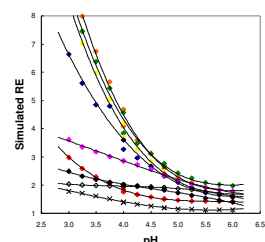
Plotting simulated RE-values (Hirokawa et al., 1983) against the pH of the lead suggests that a "separation according to pKa" at low pH-values should be more effective than a "separation according to mobility", as co-migration of analytes in mixed zones is becoming more likely with increasing pH.
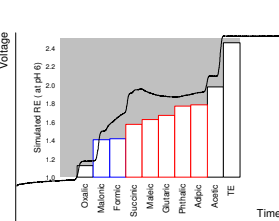
At pH 6 the RE simulation indicates that several acids are inseparable (differences in RE are too small), which is evident experimentally:

Bar graph of simulated RE-values at pH 6 overlaid with isotachopherogram (black trace) of the nine acids (LE: HCl 5 mM, adjusted to pH 6 with histidine, 0.1% MHEC; TE: Nicotinic acid).
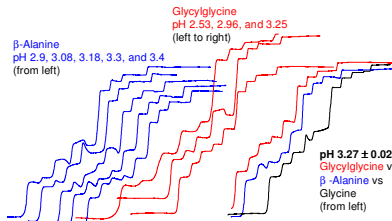
Between pH 2.5 and 3.5 various concentrations of the leading ion (10, 5, 1, and 0.5 mM), and different counter ions were evaluated.

With increasing pH, the steps become sharper (and separation times decrease), but separation of acetic and adipic acid remains problematic.
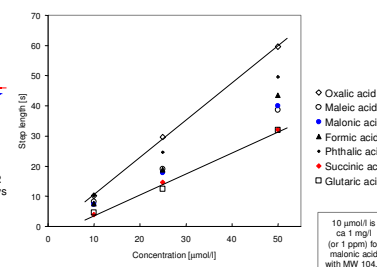
With detection limits below 10 μM (ca 1 ppm or mg/l), the sensitivity of our current method (HCl 5 mM, Gly-Gly to pH 3.5) is comparable to that of published CZE methods (Adler et al., 2003; Soga and Ross, 1997 -- see Table 1 below).

Table 1. Concentration of a 10 μM standard mixture vs detection limits of CZE and IC methods reported in the literature (all values in mg/l [or ppm]).

	CZE Soga & Ross, 1997	CZE Adler et al., 2003	ITP	CZE Dabek-Zlotorzynska et al., 2001	IC Dabek-Zlotorzynska et al., 2001
Oxalic	1.8	3.0	1.2	0.075	0.003
Malonic	.	3.4	1.0	0.069	nd
Succinic	1.2	2.0	1.2	0.054	0.014
Phthalic	.	.	1.6	0.110	0.014
Glutaric	.	2.4	1.3	0.072	0.009
Adipic	.	3.0	1.4	.	.
Maleic	.	.	1.2	.	.
Formic	1.0	.	0.7	0.052	0.008
Acetic	0.9	.	0.8	0.047	0.009

Real-Life Samples

With the current method, separation of acetic and adipic acid is not entirely satisfactory, and some other analytes that are potentially present in APM have not yet been examined (for example, the higher diacids, which would require a slower TE, or the two isomers of phthalic acid).

With this in mind, it was decided that some real APM samples should be analyzed before developing the method further.

The time axis for Filter 025, all others have been shifted (and more so than it may appear...).

Isotachopherograms from the 2nd (analytical) column of five filter extracts (130 μl injections), compared with two standard mixtures. Note the long step of excess inorganic phosphate with formic acid co-migrating. Oxalic acid is clearly visible as the main organic anion in all five samples.

Filter 024 is different from the others in that there is an additional step (a contaminant ?) before oxalate, and a markedly slower 'slope' after phosphate. There is some evidence for the presence of phthalate, succinate, and possibly glutarate and adipate, but a higher sensitivity and/or a pre-concentration step are needed to confirm this.

Table 2. Oxalic acid concentrations in APM.

	In the Extracts [mg/l]	In Air [μg/m³]
Filter 025	0.8	0.18
Filter 026	1.1	0.23
Filter 027	1.0	0.22
Filter 028	0.9	0.18
Filter 024	1.2	0.25

A quantitative estimate (Table 2), based on a limited number of parallel standard injections, indicates oxalic acid levels of ca 0.8 – 1.2 ppm in the water extracts, equivalent to ca 180 – 250 ng per cubic meter of air. These values are in excellent agreement with data published for other urban sampling sites (e. g., Rohrl and Lammel, 2001).

Conclusions and Future Plans

The sensitivity achievable with isotachophoresis was found to be comparable to that of published CZE methods, with lower detection limits anticipated with further optimisation.

In future investigations we will examine:

- larger injection volumes (300 μl);

- slower TE ions for the higher diacids;

- concentration cascades to accelerate the removal of the inorganic ions -- or use dithionate as LE to simultaneously determine inorganic anions in the pre-separation column;

- three-dimensional ITP (using a 2nd analytical column and different LEs in series to obtain different selectivity for 'difficult' pairs of ions);

- combination of an ITP pre-concentration step with CZE separation for lower detection limits.

Ultimately, hyphenation with MS is clearly needed to enable positive identification of compounds.

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Experimental

Separations were performed with the three-dimensional CE-instrument described by Hanna et al. (2000) using a 0.8 mm (i.d.) x 90 mm pre-separation column (FEP), and a 0.3 mm x 200 mm analytical column (quartz).

LE: HCl, various concentrations (10, 5, 1, and 0.5 mM), and counter ions (β-alanine, glycylglycine, and glycine) were evaluated at pH-values between 2.5 and 3.5 (and at 6.0).

The current method uses HCl 5 mM, adjusted to pH 3.5 with glycylglycine. (No polymers were added to reduce EOF, as there was no noticeable improvement at low pH.)

TE: 5 mM Nicotinic acid, or caproic (hexanoic) acid

Currents: 180 μA (pre-separation), 36 μA in the analytical column

Injection volumes: 30 μl and 130 μl

Detection: Contactless conductivity

The PM10 Particulate samples analysed were from the Marylebone Road / Baker Street sampling site in central London; the filters were extracted with 5.0 ml of water by sonicating for 30 min, centrifuged, and filtered with 0.2 μm syringe filters.

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