

AN ION CHROMATOGRAPH FOR EXTRATERRESTRIAL EXPLORATIONS.

P. K. Dasgupta¹, W. Huang¹, B. N. Stamos², M. Zhang,¹ Y. Bedoustani,¹ A. C. Noell,² and A. Davila³

¹Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington Texas 76019-0065 (Dasgupta@uta.edu), ² Jet Propulsion Laboratory, 4800 Oak Grove Dr. MS 183-401 Pasadena, CA 91109, ³ SETI Institute, NASA Ames Research Center. MS 245-3, Moffett Field, CA 95136

Introduction: Ion chromatography (IC) is the benchmark technique for ion analysis. Recent technological developments allow us to build small and compact IC prototypes that can make key contributions in a variety of areas in planetary exploration, including investigations of inorganic and organic chemistry, habitability, and even the search for evidence of life [1]. For example, the surprising detection of perchlorate in Martian soil demonstrated both the importance of performing soluble ion measurements and the need for improved instrumentation to unambiguously identify all of the species present. Versatile designs and operational simplicity make *in situ* IC suitable for multiple spacecraft configurations and mission classes, including landers, rovers, and orbiters to planets, asteroids or icy moons.

IC vs. CE: Present day commercial ion chromatographs are far too bulky and power consuming to be directly considered. In addition, current technology relies on particle packed columns that must be kept wet and unfrozen even when they are not used to perform reliably. For this reason, many researchers have advocated electrophoresis, both in the microchip and the traditional capillary format. Capillary/ μ chip electrophoresis (CE) can provide extraordinarily efficient high speed separations under ideal circumstances but its Achilles heel is lack of robustness. Any adsorption of injected material on the wall changes flow and makes future separations unpredictable and analyte identification tenuous, if not impossible. In the 90's, after Waters introduced a "Capillary Ion Analyzer" system demonstrating excellent separation performance, several other manufacturers introduced similar instrumentation. Suffice it to say that the entire breed has now become extinct.

Open Tubular Ion Chromatography (OTIC): Much of the benefits of CE can be realized in ion chromatography in an open tubular format. The columns can be dried and frozen and wetted and reused. However, whereas CE is typically carried out in 50-75 μ m bore columns, open tubular liquid chromatography at these radial dimensions is inefficient. The mass transfer efficiency to the wall depends on the inverse square of the inner diameter, as

such, even small changes in diameter can have a large effect.

As Jorgenson, the father of capillary zone electrophoresis, famously quipped, *CE is a wonderful technique, except it has three small problems: Injection, Separation and Detection*, this triad of Jorgenson problems exponentially increase with decreasing column bore. In addition, in OTIC, unlike CE, it not sufficient to have a narrow bore tube, the walls of that tube must be appropriately functionalized. Carrying out chemistry within sub-50 μ m bore tubes without blocking them is not a high yield process.

Current Progress: In last several years, aided by generous sponsorship from NASA first through an ASTID and now through a PICASSO grant, we have made significant progress towards a miniature IC in the OT format that can be powered by a pneumatic pump (under 100 psi, 7 bars, often as low as 2 bars), that uses flow rates in the 10's to a few hundred nL/min with injected volumes in the pL-nL range and can separate and detect many analyte ions, both organic and inorganic, in the sub- to single-digit μ M levels. Our experience indicates that the conflicting demands of functionalizing walls and sensitive detection vs. separation efficiency reaches an optimum compromise in the 10-30 μ m column diameter range. The system operates off a pressure source like a keyboard duster via a miniature digital pressure controller. It uses a set of miniature solenoid valves governed by a Cypress Semiconductor System on a Chip (SoIC, PSoC5) to perform variable volume injections (as small as 40 pL for a 19 μ m bore column up to the entire column volume) with a reproducibility of $\pm 2\%$ and with very little dependence on the sample viscosity. While we started with silica columns, the eventual goal being suppressed anion chromatography which uses alkaline eluents, we needed to use polymeric columns that are stable in strong base. We have had thence fabricated capillaries from polymethylmethacrylate, and cyclic olefin polymers (COP) and copolymers. We chemically treated the interior surface of these capillaries to endow them with carboxylic acid or sulfonic acid groups and then coated them with a suspension of anion exchanger latex nanoparticles, the same types as commercial packed columns so that extant separation protocols can be readily transferred. Special procedures had to be

developed to quantitatively measure the capacity of these columns (low nanoequivalents) [2]. Detection in such small capillaries proved to be the biggest challenge as none of the extant commercial contactless conductivity detectors produced consistent or meaningful responses. An extensive effort towards theoretically understanding the behavior of such detectors through modeling and simulation led us to the conclusion that one must operate at an altogether much lower excitation frequency domain to be successful [3]. These findings and appropriate electronic design led to the development of a simple, compact detector that could even be used in capillaries as small as $2\ \mu\text{m}$ in bore [4]. The pneumatic eluent delivery and injection systems, coupled to latex coated polymeric capillary columns led then to complete ion chromatograph [5]. A sub-3 kg, sub-watt portable OTIC, field tested once in the Atacama Desert, is presently being refined for a second, more rigorous testing. Meanwhile the cyclic olefin polymer (COP) OTIC columns (these can be coiled into small diameter coils, increasing column efficiency, already reaching 150,000 plates/m in favorable cases) and their sulfonation conditions have been thoroughly characterized. Finally we have been able to fabricate electroalytic suppressors small enough to be coupled to $28\ \mu\text{m}$ bore columns without measurable loss of efficiency (suppressor size must be further reduced to work properly with $19\ \mu\text{m}$ bore columns) that now permit hydroxide eluent gradient IC with performance unequaled by any commercial IC available today.

Presently we are attempting to develop a small enough pulsed amperometric detector and carry out amino acid separations in this format.

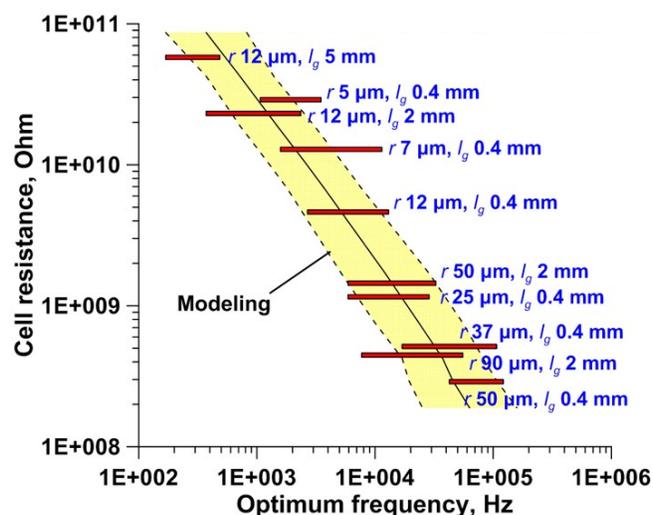


Figure 1. The river of optimum frequency. l_g is the gap between the probe electrodes, $2r$ is the capillary bore.

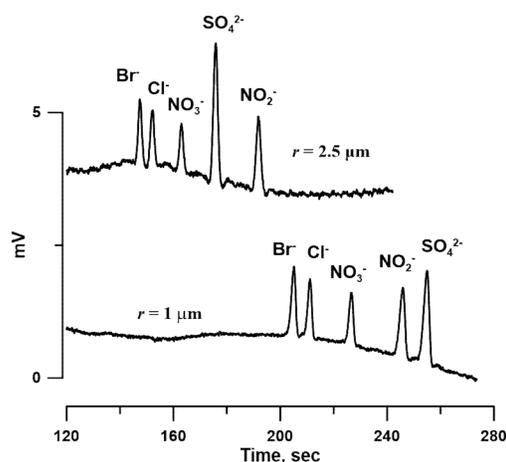


Figure 2. Capillary Electrophoresis in very small capillaries with new admittance detector.

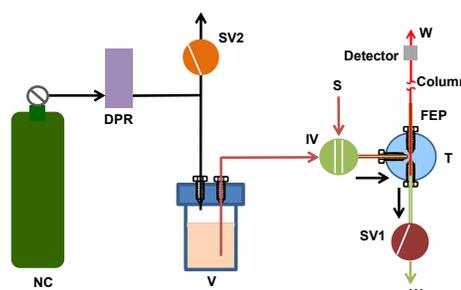


Figure 3. Operational Schematic of OTIC.

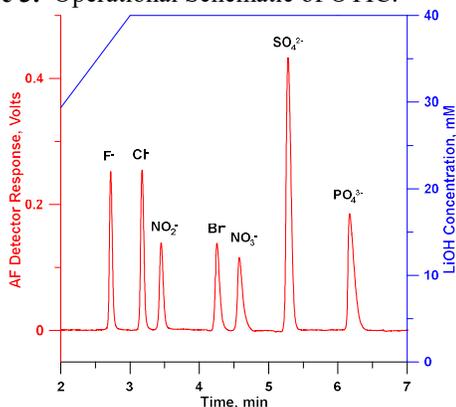


Figure 4. Gradient suppressed OTIC on a 75 cm $28\ \mu\text{m}$ column, $100\ \mu\text{M}$ each analyte, phosphate $200\ \mu\text{M}$, $6.7\ \text{nL}$.

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