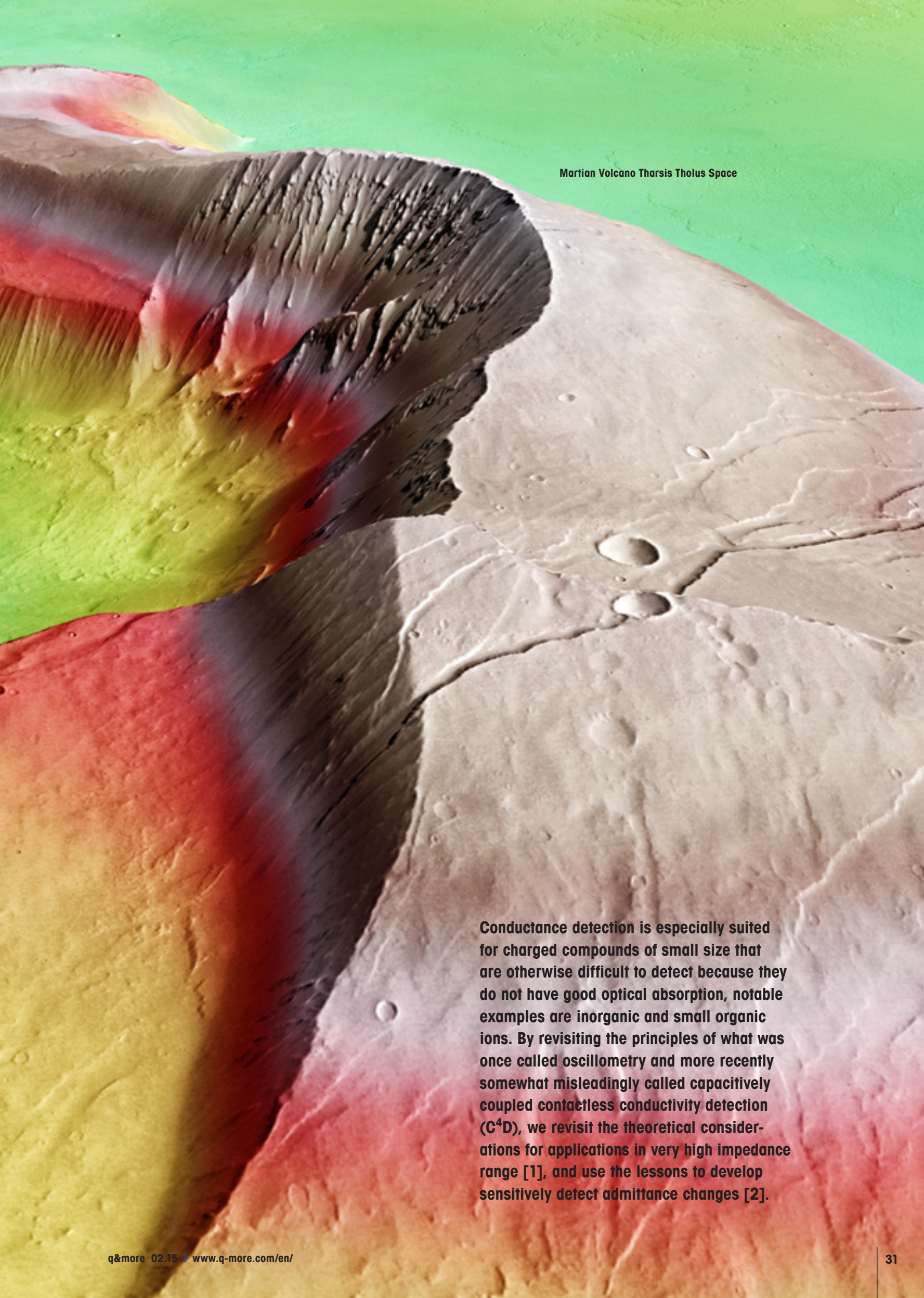


Conductance or admittance?

Admittance detector: Exploration for high impedance capillary systems

Dr. Min Zhang and Prof. Dr. Purnendu K. Dasgupta
Department of Chemistry and Biochemistry, University of Texas at Arlington, USA



Martian Volcano Tharsis Tholus Space

Conductance detection is especially suited for charged compounds of small size that are otherwise difficult to detect because they do not have good optical absorption, notable examples are inorganic and small organic ions. By revisiting the principles of what was once called oscillometry and more recently somewhat misleadingly called capacitively coupled contactless conductivity detection (C⁴D), we revisit the theoretical considerations for applications in very high impedance range [1], and use the lessons to develop sensitively detect admittance changes [2].

Probing electrical properties through an insulating wall

Techniques that probe the electrical properties (permittivity or conductivity) of a medium through an insulating wall using alternating excitation can be traced back to 1940s. The 1952 benchmark instrument was the Sargent Model V Oscillometer [3]: Operating at a frequency of 5 MHz, it could detect dielectric constant changes of 0.0003 units and could monitor conductometric titrations at concentrations less than about 0.01 M. An oscillometric flow-through four – electrode detector was developed in the 1980's for capillary scale isotachopheresis [4]. By and large, however, oscillometry fell out of the horizons of scientific utility.

With the introduction of capillary zone electrophoresis (CE) in the 90's, the needs for sensitive detection methods that could work at this scale, became acute. Conductance detection was of particular interest as unlike optical detection, there are no downscaling penalties in conductivity detection when transferring to the capillary scale. Although some methods were developed where the probe electrodes touched the solution, making contact in small capillaries was non-trivial and sensitive measurement in an extant high voltage field was difficult. Zemann et al. [5] and da Silva and do Lago [6] independently introduced the adaptation of an oscillometric detection technique for CE with two tubular/ring electrodes placed on the capillary a small distance apart (see fig. 1). While Zemann et al. [5] first coined the term capacitively coupled conductivity detection (originally abbreviated as CCCD) and later, “contactless” was further added, the current most common acronym being C⁴D. As can be seen in figure 1, two ring electrodes are separated by a short distance along a capillary. An alternating voltage is applied to the first electrode. The wall acts as a capacitor so the field is coupled to the solution inside, it travels through the resistance represented by the solution, and is then coupled again capacitively through the wall to the second electrode where it is picked up, amplified and rectified. Under the right circumstances (as the wall capacitive reactance remains the same) the overall current can be linearly related to the solution specific conductance (σ) over a small range of σ . Commonly recognized advantages of C⁴D are its simplicity and low cost, its ability to monitor the solution electrical properties noninvasively on-column, the ability to respond to all charged species, and freedom from electrode fouling. Presently, several commercial C⁴D detectors are available and are widely accepted.

Anomalous response of a C⁴D and admittance detection

With rare exceptions, such detectors have been used with relatively conductive solutions ($\sigma \geq 200 \mu\text{S}/\text{cm}$) and/or with capillaries with inner diameters $\geq 25 \mu\text{m}$ (majority $\geq 50 \mu\text{m}$), typical of capillary electrophoresis (CE). While a linear response with the analyte concentration is generally reported, some authors had noted that the response slope can become zero or even negative in a lower σ range. We have been interested in (suppressed) open tubular ion chromatography (OTIC), preferably in columns of $<20 \mu\text{m}$ ID. In suppressed conductometric chromatography or suppressed CE [7], the background σ is very low. Even in nonsuppressed systems, good limits of detection (LODs) require low to modest background σ . Small diameters and low σ (or both) represent a generally unexplored territory. In addition, we discovered to our surprise that a commercial C⁴D (available commercial detectors permit operations in the 38 – 612 and 50 – 1200 kHz range) can produce completely anomalous response in this domain or over large spans of σ . (see fig. 2).

The present article explains why this behavior should have been expected from the outset and to argue that perhaps this stems from the inappropriate nomenclature of calling devices that really measure the *admittance* as *conductance* detectors. Further we show that when this fog of understanding is removed, even with very simple circuits operation in tailored frequency domains results in performance never previously attained.

At least one other group has also recognized this inappropriate name and have decided to refer to such a general class of detectors as “*contactless*” impedance detection [8]. We prefer *admittance* over *impedance*, since the primary measured variable is current; in much the same way as we refer to a conductivity detector rather than a resistivity detector. In addition, the admittance signal does include effects of the wall with which the electrodes are very much in contact. The term *contactless* admittance or impedance thus seems inappropriate. While the name may be too catchy or perhaps now too entrenched to be replaced, a C⁴D is not what its name indicates it is. However, it is fair to say in Shakespearian zest, What's in a name? In many instances, the virtues of the device cannot be matched by a standard conductivity detector.

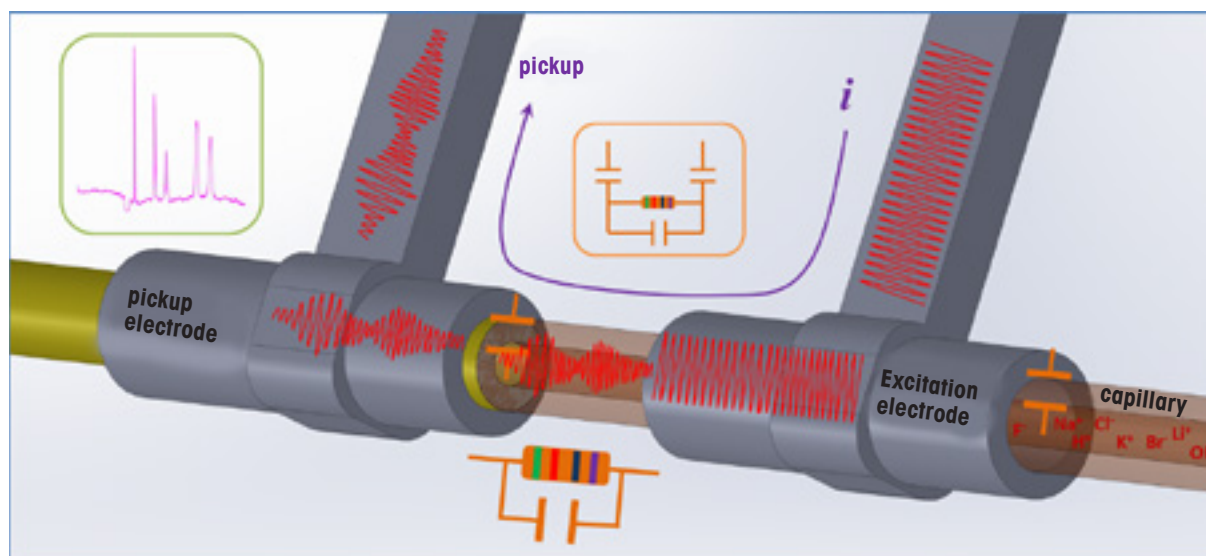


Fig. 1 Detection cell configuration and equivalent circuit

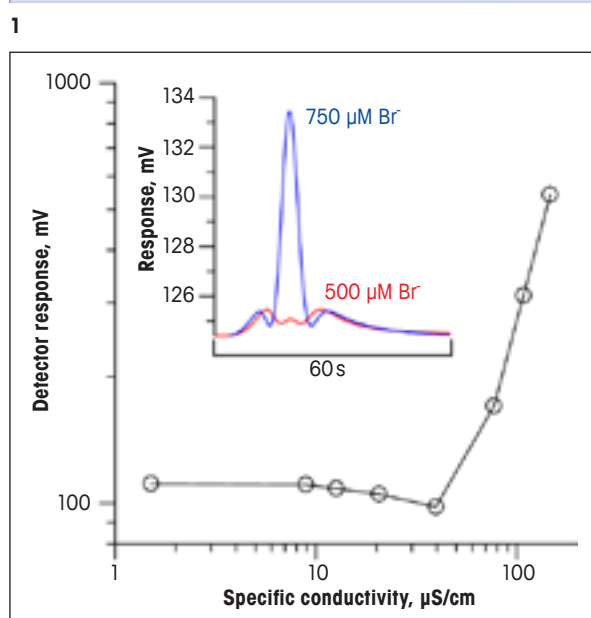


Fig. 2 Calibration curve obtained by flowing KCl solution of different concentrations first through a conductivity detector and then through a PMMA capillary ($r_o = 170 \mu\text{m}$, $r = 8 \mu\text{m}$) with a commercial admittance detector [1]. The insert is chromatographic response to injections of 0.5 and 0.75 mM Br- from a suppressed Dionex IC, a portion of the suppressor effluent was spilt through the above PMMA capillary. Commercial detector 150 kHz, gain 200%, Attenuation 0 dB. The batwing feature and abrupt change in response is common.

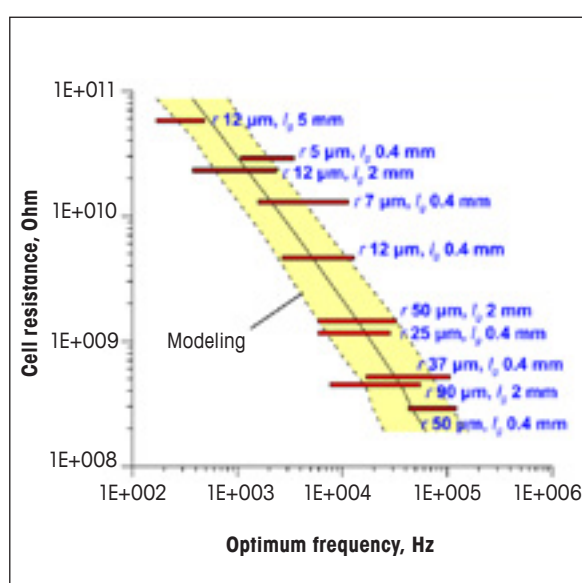


Fig. 3 Comparison of optimum frequencies for various values of R_{cell} for different capillaries [1]. Within the optimum frequency range, the net response of an electrolyte sample (here 0.1 mM KCl) in pure water background (18 M Ω), is larger than 80% of its maximum.

Equivalent circuit model and optimum frequency

To explain the behavior of admittance detector, we investigated, both theoretically and experimentally, capillaries with inner radii (r) of 5 – 160 μm and $\sigma \approx 1 - 1400 \mu\text{S/cm}$, resulting in cell resistances of 51 G Ω to 176 k Ω [1]. The equivalent model we used is a discrete element model (DEM), wherein the capacitors and resistors in figure 1 are divided into a multitude of RC elements in a network. In our DEM, the solution interrogated represents not only a resistor; it is also a dielectric with a finite capacitance (C_{aq}) that is in parallel with the resistor. This capacitance has largely been ignored in other models. Actually, as the conductance of the resistive component and the admittance of the capacitive component are in parallel and they both scale in the same fashion with the capillary radius (r) or the interelectrode gap (l_g), as a first approximation, the ratio of the current that flows through the capacitive component versus the resistive component is not dependent on r or l_g but solely on σ and the excitation frequency (f). As σ decreases and f increases, more of the current flows through the capacitive component, making the system insensitive to σ . Moreover, at low electrolyte

concentrations, the dielectric constant actually decreases as the electrolyte concentration increases, resulting in a decrease in C_{aq} . In many cases, especially at low σ and higher f , the current through the cell can decrease with as the cell conductance, i.e., σ , increases.

The DEM simulations show good qualitative agreement with experimental results and correctly predict the negative response behavior observed under certain conditions. It would be apparent that the optimum frequency for detection will be dependent both on the background conductance itself and r . Figure 3 gives the optimum response frequency range plotted for various values of cell resistance (R_{cell}) and compares this with what is observed experimentally. The optimum frequency range decreases with decreasing background σ , the capillary bore and increasing electrode gap; all three contribute to a greater R_{cell} . The optimum f for $r < 15 \mu\text{m}$ is much lower (<20 kHz) than most relevant publications. As the optimum frequency decreases, so does the response slope. However, it is still possible to achieve sensitive detection if external noise can be minimized and an adequate degree of amplification is possible. Another lesson is that a frequency which results in the greatest current from a background solution of given



Fig. 6 Brian Stamos testing soil extract at the Atacama Desert in Chile with a prototype OTIC instrument equipped with a low frequency admittance detector.

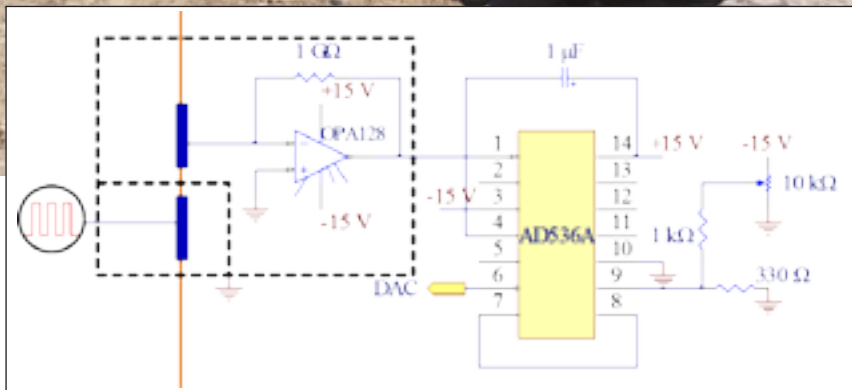


Fig. 4 Schematic diagram of the admittance detector

σ may not be the best frequency to detect small changes in σ against that background

Exploration for high impedance systems with low frequency admittance detector

Based on the discussion above, we constructed an admittance detector for high impedance systems (small capillary bore and/or low solution specific conductance) [2]. According to the model, the probe frequency must be relatively low for high impedance systems. The detector schematic diagram is illustrated in figure 4. A low bias current operational amplifier in the transimpedance configuration permitted high gain (1 V/nA) to measure pA–nA level currents in the detection cell. Aside from an oscillator, an offset-capable RMS-DC converter formed the complete detection circuitry. Operation at a low frequency (≤ 1 kHz) provided the best response to conductance changes in capillaries ≤ 20 μm in bore.

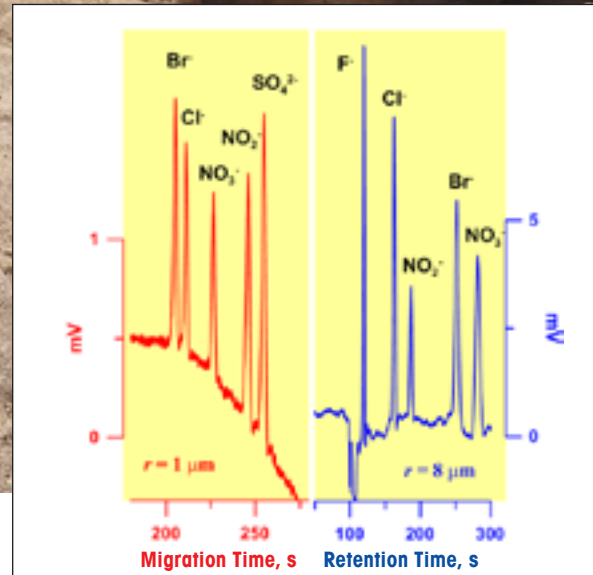
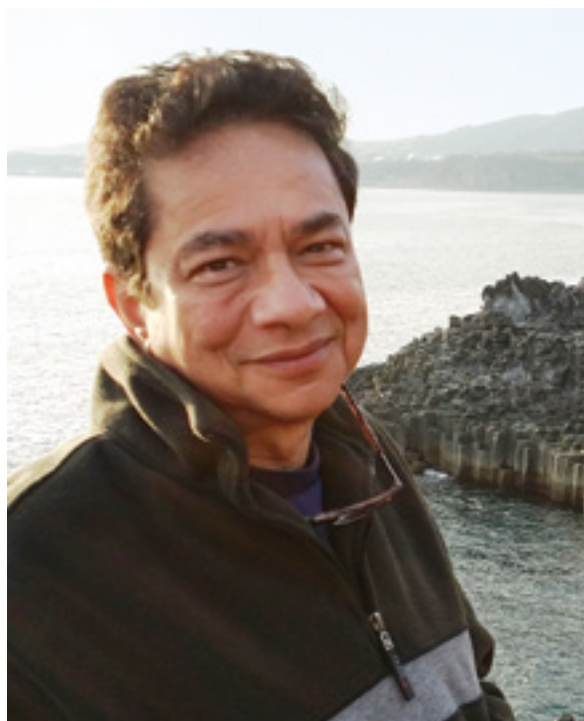
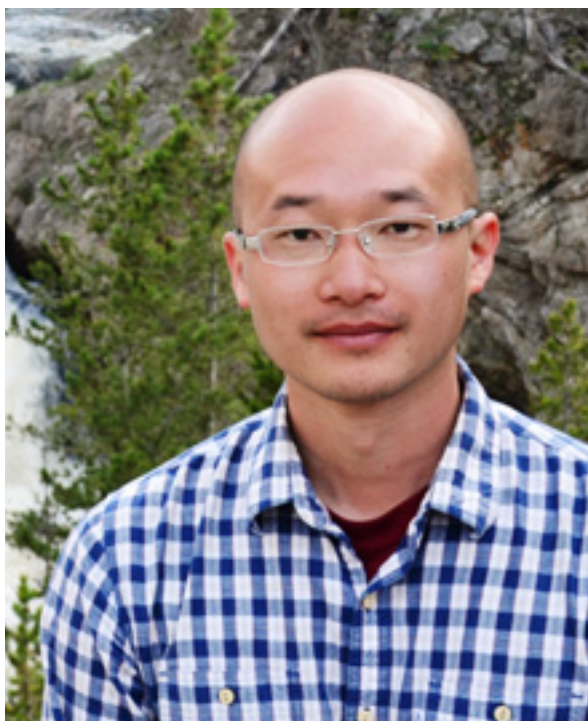


Fig. 5 Application of admittance detector for high impedance systems [2]. Left, CE, $r, r_o = 1 \mu\text{m}, 75 \mu\text{m}, 50 \text{cm}$ length, 42 cm separation length. Sample, 100 μM NO_2^- , 50 μM Cl^- , Br^- , NO_3^- , and SO_4^{2-} ; BGE, 12 mM His adjusted to pH 4 with HOAc, injection: 46 fL (7.4 μm) for 2 μm i.d. Separation voltage: -15 kV, $V_{\text{app,p-p}} = 22$ V; $f = 1$ kHz. TIA gain 1 V/nA. Right, OTIC, $r, r_o = 8 \mu\text{m}, 170 \mu\text{m}$; 45 cm long, AS18 latex coated PMMA capillary; effective length 40 cm; sample, 200 μM each anion, 0.41 nL; eluent, 1 mM sodium benzoate; flow rate, 45 nL/min; $V_{\text{app,p-p}} = 22$ V; TIA 1 V/nA.

The detector was applied to various high impedance systems (see fig. 5). LODs of KCl scaled inversely with the capillary cross section and were 2.1 and 0.32 μM injected KCl for $r = 1$ and 2.5 μm capillaries, respectively. When used as a detector on an $r = 8 \mu\text{m}$ bore poly(methyl methacrylate) capillary in a split effluent stream from a suppressed macroscale ion chromatograph, the LOD was 27 nM bromide compared to 14 nM observed with a state of the art commercial bipolar pulse macroscale conductivity detector with an actively thermostated cell, with the actual probe volumes being more than 6 orders of magnitude smaller for the capillary. We also show applications of the detector in electrophoresis in capillaries with $r = 1$ and 2.5 μm . Efficient heat dissipation permits high concentrations of the background electrolyte and sensitive detection because of efficient electrostacking.

Future application

An effort to develop a capillary scale open tubular ion chromatograph (OTIC) for extraterrestrial explorations is ongoing in our group. Confirming the presence of



Min Zhang, studied environmental science at Xiamen University, China, receiving his Ph.D. there in 2011. This was followed by a post-doc at the University of Texas at Arlington in the USA from 2012 to mid-2014. During this period, he participated in a project developing capillary scale ion chromatograph and detector for the same. Now, he is a postdoctoral research associate at the University of Tasmania, Australia mainly working on miniaturized separation instruments.

Purnendu K. (Sandy) Dasgupta, is the Hamish Small Chair in Ion Analysis at the University of Texas at Arlington. Born in India, Sandy has spent virtually all his adult life in the US, specifically Baton Rouge, Louisiana (where he got his PhD), Davis, California (where he worked as an Aerosol Research Chemist and taught Environmental Engineering), Lubbock, Texas (where he spent 25 years at Texas Tech), and most recently since late 2006, Arlington, TX, which he now calls home. Sandy has had training both in electrical engineering and analytical chemistry; his first love is building instruments. Although he has acquired some distinction for his work in chromatography, particularly ion chromatography, he keeps fleeing from this to that – at heart he is just a tinkerer. The current flagship project in the lab is a NASA sponsored effort to build an ion chromatograph for extraterrestrial explorations. He is both an IEEE fellow and a recipient of American Chemical Society awards in Chromatography and Chemical Education.

perchlorate and mapping its occurrence on Mars [9] has become an essential prelude to manned missions to Mars. Perchlorate represents an easily accessible source of both oxygen and energy, of great potential importance to any future manned station while at the same time one must also be conscious of the adverse effects of exposure to perchlorate. Ion chromatography has always been the most reliable method for the measurement of perchlorate. To fulfill such a task, traditional packed columns are not desirable. The ambient temperature in Mars ranges between -15 and -100 °C, with power availability always being at a premium, it is not convenient to keep an instrument heated when it is not in use. But packed columns are not likely to survive repeated freeze-thaw cycles. Open tubular columns operate at a lower pressure and readily survive drying and freezing and rewetting. However, for OTIC to be efficient, it must be conducted in very small bore capillaries. Present efforts are to fabricate suppressors that are of sufficiently small size to match these capillaries. In this case we have the desired very

low background σ and in a very small capillary making sensitive detection by traditional “C⁴D” devices impossible. The successful application of the low frequency admittance detector for high impedance applications removes the limitation. We have reported an OTIC [10], and a portable, miniaturized version of this instrument has been tested in Atacama Desert, the driest place on this planet (see fig. 6).

■ dasgupta@uta.edu

Bibliography

- [1] Zhang, M. et al. (2014) *Anal. Chem.* 86, 11548–11546
- [2] Zhang, M. et al. (2014) *Anal. Chem.* 86, 11547–11553
- [3] E. H. Sargent & Co. (1952) *Anal. Chem.* 24, 19A
- [4] Gaš, B. et al. (1980) *J. Chromatogr. A* 192, 253–257
- [5] Zemmann, A. J. et al. (1998) *Anal. Chem.* 70, 563–567
- [6] Fracassi da Silva, J. A. & do Lago, C. L. (1998) *Anal. Chem.* 70, 4339–4343
- [7] Dasgupta, P. K. & Bao, L. (1993) *Anal. Chem.* 65, 1003–1011
- [8] Opekar, F. et al. (2013) *Sensors* 13, 2786–2801
- [9] Hecht, M. H. et al. (2009) *Science* 325, 64–67
- [10] Yang, B. et al. (2014) *Anal. Chem.* 86, 11554–11561

Photo: ESA/DLR/FU Berlin (G. Neukum)



The article is also available online from the q&more Portal

■ www.bit.ly/qmore-1502-4