P rofessor Sandy Dasgupta recounts the history of his involvement in ion chromatography (IC) and his pioneering work in electrolytic eluent generation and electrolytic suppression in IC. He also discusses his current project, a NASA-sponsored undertaking to develop a miniature, low-power, low-eluent consumption IC instrument for the Mars exploration program and investigate the possible existence of life on this planet.

**LCGC:** Tell us about your contributions to key developments in ion chromatography, including electrolytic eluent generation and electrolytic suppression.

**Dasgupta:** In my late 20s in my first professional job at the University of California, Davis, our lab was among the first to acquire an ion chromatograph. My first chromatograph was the Dionex Model 10, with a serial number of 7. It was a very simple machine — I could tear it apart and build it back up, which I cannot do with modern instruments.

At that time, ion chromatography required stopping and regenerating the suppressor every so often. You had to take it offline, bring in another one, and regenerate the offline suppressor, which was a significant inconvenience.

A group of scientists at Dow Chemical — Hamish Small, Tim Stevens, and Ted Miller, and I independently — arrived at the same idea at about the same time: To use a membrane tube, bathe it with acid on the outside, and flow the eluent inside it. This device accomplished ion exchange in much the same way a packed column did except that it was never exhausted — it was continuously regenerated.

The Dow group published the first paper on the “continuous tubular suppressor,” but our group at Texas Tech developed a better design, which was later patented, in which filaments are put inside the membrane tubes and coiled.

I realized that there were two bottlenecks with the ion transport process using a membrane: transporting the ions to the membrane and transporting the ions through the membrane. Ideally the rate-limiting step should be the latter.

It occurred to me that I could augment ion transport if I applied an electric field. This process became the basis of electrodialytic suppression, which is in wide use today. Electrodialytic suppression allows continuous use, and it has the advantage of using water rather than chemicals to accomplish regeneration. For a KOH eluent, the process removes $K^+$ from the eluent to the negative electrode chamber where it reacts with water and makes KOH and hydrogen gas.

Early on I decided hydroxide was the best eluent because it can be suppressed to water. Any other eluent when suppressed will have a finite conductance that changes with the eluent concentration in a gradient. However, hydroxide in pure form is elusive because it immediately scavenge $CO_2$ from air and generates carbonate. Hydroxide and carbonate have very different eluent strengths, and you quickly find that the retention of all your ions is decreasing because the hydroxide eluent is changing to carbonate.

It occurred to me that the KOH I make on the cathode side of a suppressor is highly pure. Unlike a suppressor I do not have to remove all the $K^+$ from the donor side, the amount of $K^+$ transported and therefore the concentration of KOH generated is directly proportional to the current. Thus, electrolytic eluent generation became the best option — and it still is today — with the eluent or mobile phase being made in situ from pure water.

**LCGC:** Can you tell us about your work on the development of chip-scale instruments?

**Dasgupta:** My involvement in developing a miniaturized instrument derived from NASA’s desire to do ion chromatographic analysis in situ on Mars. The only wet experiment in Mars previously done was in 2008 with the Phoenix lander. Soil was put in a glorified beaker that had ion-selective electrodes embedded on the walls. After adding water and stirring, the electrodes took the reading and sent the results back to Earth.

Ion-selective electrodes are not specific. You may think you are measuring one thing and find out that you really measured something else. The experiment used 1.5 g of soil per beaker and the nitrate electrode reported back that there were 2 g of nitrate, which was clearly absurd!
At this point, NASA scientists on earth quickly determined that the electrode responded much more to perchlorate than it did to nitrate. The eventual publication indicated that Martian soil may contain half a percent perchlorate, on average, which caused quite a stir. Perchlorate is a wonderful energy source. When heated, perchlorate decomposes, liberating chloride and oxygen. This means one has an easily tapped source of oxygen and heat. If I want to start a station on Mars, what could be better than that?

The other significance of perchlorate discovery is connected to the possibility of existence of organics. In the mid-70s, the Viking spacecraft was looking for organics on Mars. The idea was that, if organic matter existed, you could take dirt, heat it up, and use a gas chromatograph–mass spectrometer to determine the composition.

Viking 1 reported carbon dioxide, water, and traces of methyl chloride and dichloromethane. The carbon dioxide and water made sense, but people didn’t understand the source of the methyl chloride and dichloromethane. They were originally attributed to terrestrial contamination, even though the Earth-bound blanks were clean. A few weeks later, Viking 2 landed on a different part of the planet and reported the exact same findings, suggesting that the methyl chloride and dichloromethane probably were not due to contamination.

Once this tentative discovery of perchlorate was made, somebody thought to take some good old Earth soil, add 2% perchlorate to it, heat it up, and to see what came off. And, what came off were carbon dioxide, water, and traces of methyl chloride and dichloromethane. Although the original data indicated no organic matter, the same results were now being interpreted that as there are organics on Mars.

To understand Martian soil chemistry and planetary evolution, it’s vital that we understand the oxychlorine chemistry by using instruments more sophisticated than ion-selective electrodes — instruments that can look not only at perchlorate but at other chlorine-containing species, as well as other ions. An ion chromatograph is capable of directly measuring organic acids, so a miniature ion chromatograph would be ideal. This realization prompted our journey that began a few years ago.

Although the present rover, Curiosity, has a large suite of instruments, it cannot operate many at once due to power limitations. The ambient temperature on Mars is ~15 °C to ~100 °C; a normal ion chromatograph will require heating to keep the column from freezing even when the instrument is not used; this would consume too much power. We therefore decided to use an open tubular column.

Separation efficiency decreases indefinitely with decreasing column diameter, but below a certain diameter, it becomes extremely difficult to functionalize inside the column or to have enough detection sensitivity. We settled on working in the 10-30 µm region as an optimum compromise.

Let’s discuss injection, separation and detection in that order. Today, we can reproducibly inject from sub-picoliter to 100 nanoliter quantities of sample (depending on the capillary bore) with high reproducibility, reasonably independent of sample viscosity. We can vary the injection volume without any need for sample loops.

If I was conducting capillary electrophoresis in a 20 µm capillary, I could use an off-the-shelf silica capillary, but for chromatography I must functionalize the walls. In addition, we ultimately wanted to use hydroxide eluents, silica was not a good material as it dissolves in base. We therefore had capillaries fabricated from poly (methyl methacrylate) (PMMA) and cyclic olefin polymer (COP) and copolymers.

PMMA capillaries already has negatively charge surface carboxylate groups. Borrowing from Hamish Small, I learned how to sulfonate the walls of these polyolefin capillaries so they have a permanent strong negative charge. Again following Small, it was easy to attach positively charged latex particles for anion separations and far simpler than creating polymeric layers within a small capillary!

Detection was the hard part. Because the individual band volumes are so small, one doesn’t have the luxury of connecting external detectors. The on-capillary detection volume is so minute that the number of ions you are trying to detect is also equally small.

On-capillary detectors for ion analysis, called capacitively coupled contactless conductivity detectors (C4Ds) are commercially available. But they either didn’t produce a signal or produced completely anomalous signals.

The best frequency for the measurement depends on the size of the capillary and the exact conductance/composition of the solution. The commercial detectors simply could not operate at the frequency we needed. Once realized, we built simple detectors that are so sensitive that you can use capillaries as small as 2 µm in diameter and still sensitively monitor the ionic separations within them. But because of blockage, it’s not practical to use capillaries this small.

We are currently working on developing a complete, portable unit. We carried out field testing in the Atacama Desert in Chile and conducted soil analysis in situ. We are in the process of perfecting our next generation of this miniature portable instrument, which eventually will be integrated into a single compact format.

My colleagues in NASA would like to see similar platforms developed for amino acid analyzers. Ultimately, people are fascinated by space exploration. We all want to know if we are here alone. Even if it seems certain that life isn’t present on Mars currently, we wonder: Was there life on Mars? Were there at least the building blocks of life on Mars or on other planets?

For more on this subject, see “From Perchlorate in Breast Milk to Perchlorate on Mars,” Sandy Dasgupta (SETI Talks), YouTube, https://youtu.be/r-p55WLXAEL.