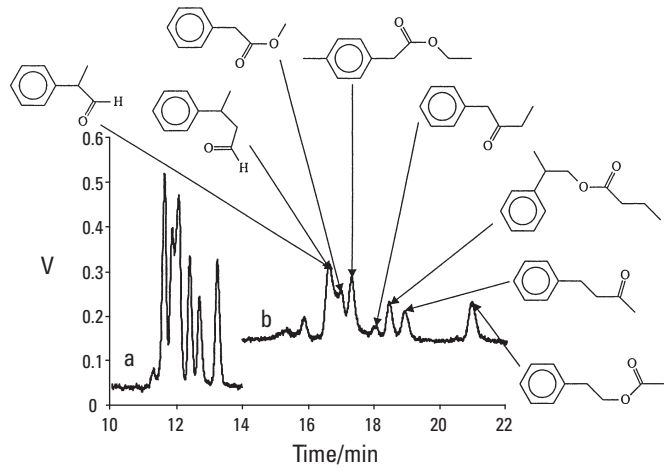
ANALYTICAL CURRENTS

CE with nonaqueous solvents

Stephen Weber and Shu Li of the University of Pittsburgh explore the largely uncharted area of CE separations of neutral compounds in nonaqueous solvents. Using lanthanide triflate salts, they successfully separate a series of closely related alcohols or oxygen-containing compounds in acetonitrile or a mixture of acetonitrile–ethylenecarbonate.

The authors believe that the lanthanide cations adsorb to the silica surfaces and the counteranions move down the column to the detector. Therefore, the injector inlet is at a negative potential (reversed polarity). Separation occurs because the solutes bind to the lanthanide ions—the stronger the binding and the higher the lanthanide concentration, the later the elution time.



Separation of oxygen-containing compounds with (a) 80-mM La triflates and (b) 100-mM La triflates in acetonitrile–ethylenecarbonate.

Changing one lanthanide for another has little effect on selectivity, but it can significantly alter retention times. Good separations are also seen when as much as 0.5% water is present. However, salt solubility is an issue. The triflates dissolve best in the acetonitrile–ethylenecarbonate solutions, with concentrations >100 mM and nearly complete dissociation.

An alternative approach is to use a fluorocarbon-modified capillary. In this system, the injector is positive, and the mobile phase contains a perfluorooctane sulfonate salt to create a small net negative charge on the wall. Alcohols strongly complexed with the lanthanide now elute first. (*J. Am. Chem. Soc.* **2000,** *122,* 3787–3788)

What the successful analytical chemist knows

How to choose a postdoctoral position, how to write a good scientific paper, where to submit those papers, what to do when giving a scientific talk, and other great career advice are found in the article entitled "How to succeed in analytical chemistry" by Charles Lucy of the University of Alberta (Canada). The article also includes numerous useful references on practical aspects of the analytical chemistry profession. Good advice is found for analytical chemists at any stage of their career. (*Talanta* **2000,** *51,* 1125–1147)

No gel required

A silicon-based nanofluidic device for separating DNA, called an entropic trap array, has recently received a great deal of media attention. So what's all the flurry about? The device, designed by H. G. Craighead and J. Han of Cornell University, has the potential to replace pulsed-field gel electrophoresis (PFGE) as the standard method for separating long DNA molecules. PFGE is slow (12–24 h), and it is difficult to extract DNA from the gels. The microfabricated device, however, does not require the use of gels or pulsed electric fields, and it has the added advantage of being able to run more than one sample at a time.

The Cornell researchers take advantage of DNA's tendency to change shape, which dictates how the molecules move through a series of constricting channels and roomy reservoirs contained on the device. These alternating thin and thick channels act as a molecular sieve. Long DNA molecules form spherical equilibrium shapes when they have enough room. However, if forced through a narrow channel, they take on a linear conformation. The width of a longer strand of DNA is the same as that of a shorter one when straightened, and both have the same head-on profile. Thus, movement through gel pores, where the DNA

Perchlorate monitoring in groundwater

Perchlorate can inhibit iodide uptake in humans, which reduces thyroid hormone production, and thus constitutes a public health concern. Perchlorate monitoring in groundwater points to industrial sources, predominantly manufacturers of rocket propellants, missiles, and fireworks. Fertilizers have also been in the news as a potential perchlorate source. It has yet to be determined, however, how widespread perchlorate contamination is. Analytical methods are needed to do that.

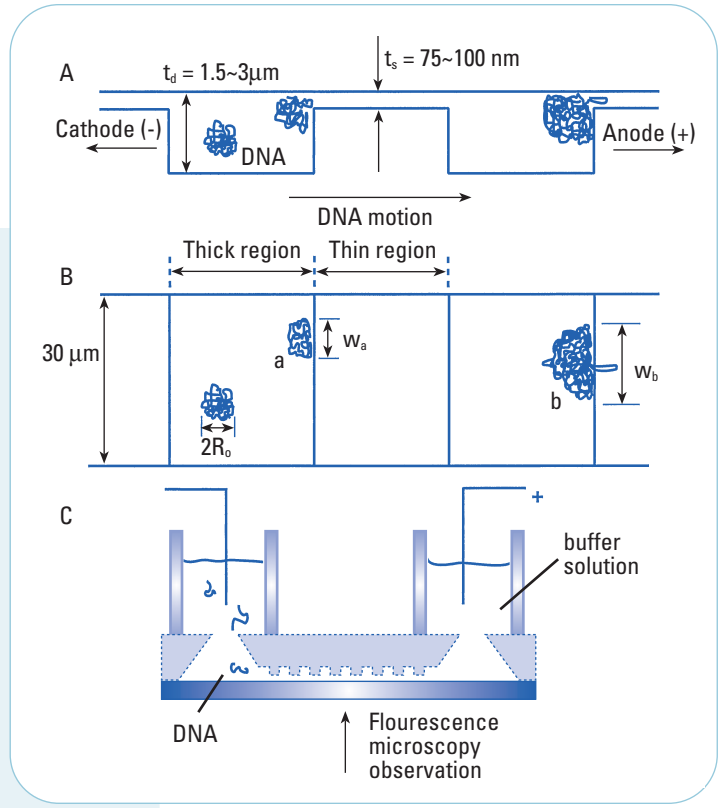
The most commonly used method for determining perchlorate levels is ion chromatography (IC) with conductivity detection. Harry R. Beller and co-workers at Lawrence Livermore National Laboratory now demonstrate that an electrospray ionization (ESI) MS/MS method offers superior detection limits and compound confirmation capabilities.

The researchers analyzed groundwater samples from the Livermore area using the ESI/MS/MS method and sent half of each sample to an independent laboratory for analysis by the state-certified IC method. The IC and ESI/MS/MS results were statistically indistinguishable when perchlorate concentrations were above the detection limits of both methods. ESI/MS/MS, however, provides greater accuracy at low concentrations, with a detection limit of 0.5 μg/L.

In addition, ESI/MS/MS has high specificity, eliminating interferences from coeluting compounds. By operating in the negative ionization mode, selective detection of ClO_4^- and ClO_3^- can be achieved. The standard additions method helps to eliminate other interferences, such as the strong signal suppression caused by sulfate, chloride, bicarbonate, and other ions abundant in groundwater. (*Environ. Sci. Tech.* **2000,** *34,* 1862–1864)

is forced into a linear conformation, is similar among strands once they reach a certain length. This is why separation is difficult with gel electrophoresis when DNA samples reach lengths of ~40,000 base pairs. With the nanofluidic device, however, strands alternately become linear and then spherical as they pass into narrow and wide spaces. With the use of fluorescent tagging and light microscopy, DNA strands are recorded as video data in order of length as they emerge.

Contrary to gel electrophoresis and intuition, longer strands finish first. This is because spherical balls of DNA float randomly and must come into contact with a narrow channel to straighten and be drawn in. Larger-sized molecules are more likely to contact a channel opening before smaller ones, so they tend to go first. When this action is repeated through a series of wells and channels, a size-dependent separation is achieved in <1 h. (*Science* **2000,** *288,* 1026–1029)



Microfabricated entropic trap array. (A) Cross-sectional view of DNA molecules being trapped when they meet a thin region. (B) Top view of the device. (C) Experimental setup. (Adapted with permission. Copyright 2000 American Association for the Advancement of Science)