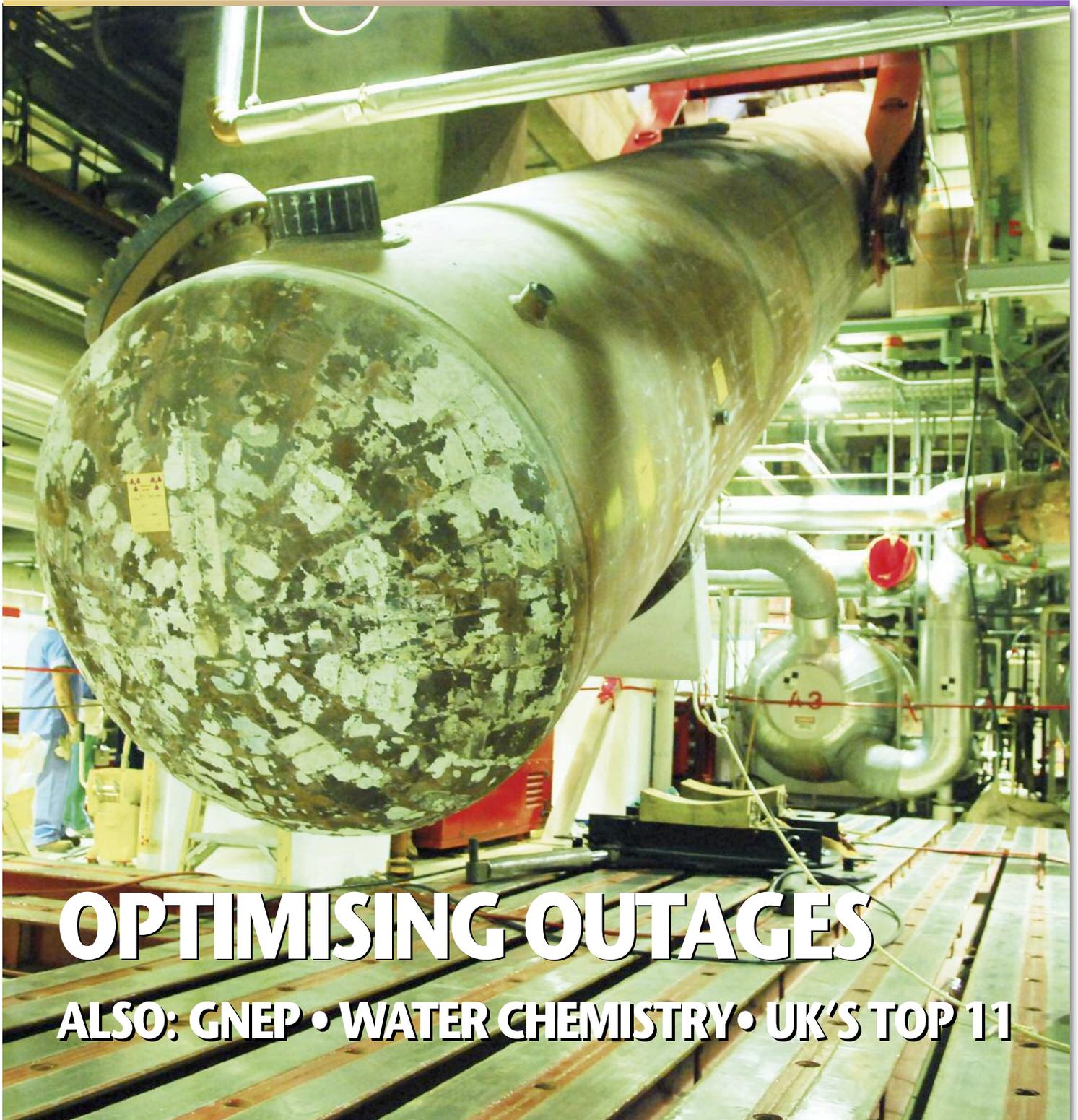


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Improving ion identification

In field tests at two BWRs, capillary electrophoresis took just minutes to detect trace levels of ions such as bromide or chloride. The technique could eventually replace conventional methods, allowing real-time analysis of water chemistry. By Paul Frattini and Susan Garcia

Successful nuclear plant operation requires careful monitoring of water chemistry, particularly in boiling water reactors, where contaminants in the reactor coolant can impact fuel performance and hamper corrosion mitigation efforts. BWR plant chemists face a difficult challenge today: how to accurately measure and analyse very low levels of ionic impurities in process streams, and how to adjust water chemistry in response.

Capillary electrophoresis (CE) presents a promising alternative to conventional methods such as ion chromatography in analysing low levels of ionic impurities, particularly

during plant transients such as start-ups, shutdowns, and impurity ingress, when multiple samples from several disparate streams require immediate analyses before plant action can be taken. While ion chromatography remains a useful tool for plant chemists, demonstrations at two US nuclear plants show that EPRI's enhanced CE technology provides several advantages, including improved detection sensitivity (without the need for pre-concentration); rapid analysis times; reduced equipment and operating costs; and reduced radwaste generation.

CE provides a sensitive detection option for measuring trace levels of ions in process streams. The basic technology, which dates to the 1960s, separates species according to their size-to-charge ratio in the interior of an electrolyte-filled capillary. By applying an electric field to initiate migration of a sample from a source location to a destination location through a capillary tube, the ionic species separate according to their electrophoretic mobility. These differences can be measured using various detectors, such as an ultraviolet (UV) device that measures absorbance differences. Separated chemical compounds appear as distinct peaks in an electropherogram.

By nature, ions are highly charged polar species that lend themselves well to CE analysis. When detection of low levels of ions that have low absorbance is desired, CE detection is commonly performed indirectly using a background electrolyte, or "probe," that contains a UV-absorbing species. Passage of the analyte, which is transparent to UV, is

then detected through displacement of the probe by the analyte.

To provide the greatest resolution and sensitivity, the size (molecular weight) per unit charge, which determines the mobility of the probe, should approximate that of the ionic species of interest.

Literature reports a number of compounds for use as CE probes, but none is entirely satisfactory for achieving the desired detection limits for ions in nuclear process streams.

To address this shortcoming, EPRI's capillary electrophoresis research focused on identifying suitable probe compounds for indirect optical CE detection of high mobility ions such as chloride, sulphate, and sodium. Cyclic vinyllogous carboxylic acids and their derivatives represent one of the most promising classes of probe compounds. These compounds display a conjugated structure of covalent bonds with resonance structures that are highly absorbing in the desired ultraviolet range [1]. An anionic member of this group, commonly known as squaric acid, is commercially available, and has been shown to be an excellent probe for anion analysis. Several cationic derivatives of the anion probe have also been synthesised (see below).

INCREASED SENSITIVITY

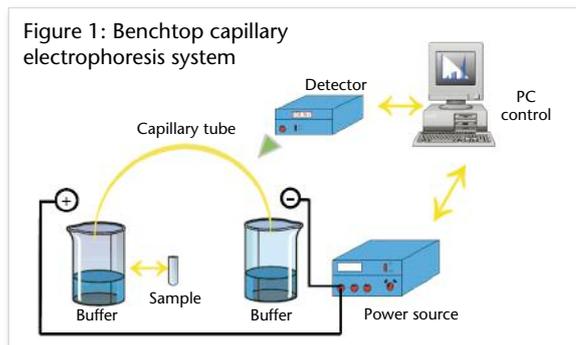
To increase the sensitivity of CE for nuclear plant applications, EPRI researchers have developed novel chemical probes for use with indirect ultraviolet optical detection [2]. Using these probes, CE is capable of rapid quantitative measurement of high mobility anions and cations at very low concentrations, making it a promising alternative to ion chromatography. For the anions of most importance to BWR plants, such as chloride and sulphate, CE can achieve resolution and sensitivity levels comparable or better than other technologies, at time scales measured in minutes rather than hours. Because chloride and sulphate impurities are known to significantly impact the rate of stress corrosion cracking, continuous monitoring and control is required in BWRs [3]. Early awareness of concentration changes can enable operators to take pre-emptive action through chemistry adjustments.

The speed at which CE measures concentration changes is a significant advantage. For example, CE technology has been able to analyse more than ten samples in the time it takes to perform a single ion chromatography analysis in a typical BWR plant. The

Anion analysis limits of detection (LOD) achieved with CE

Anion	LOD (ppb)
Bromide	2.0
Chloride	0.05
Sulphate	0.75
Nitrate	1.0
Phosphate	5.0
Fluoride	1.6

Figure 1: Benchtop capillary electrophoresis system



rapid analytical capabilities make the technology particularly well-suited for future online systems.

The personnel exposure benefits associated with CE are linked to the lower liquid waste volumes that have to be handled by technicians. Whereas pre-concentration requirements force competing systems to generate litres of ion-transporting solution called eluent, CE generates only millilitres of eluent volume.

CE technology has significantly lower capital and operating costs than comparable systems. Up front equipment costs are 2-4 times lower, while the costs for consumable items and waste disposal are also about 10 times less.

Finally, CE technology is easy to use. Preparatory work to ready the instrument prior to receiving the sample is minimal. Significantly less user attention is required to respond to items such as equipment alarms. Also, the technology is amenable to automation and future on-line configuration, further easing operator use.

FIELD DEMONSTRATIONS

Researchers demonstrated the CE analytical method at the Sheridan Training Facility of Nebraska Public Power District's Cooper Nuclear Station in May 2007. The project team resolved several analytical challenges related to CE. These results are published in an EPRI report [4].

Figure 1 shows a schematic for the benchtop CE system that has been used at US plants. The installation consisted of a Groton Biosystems GPA 100 CE instrument equipped with a Bischoff variable UV/Vis wavelength detector controlled by a Dell computer. Data was collected and analysed with DAX 8.0 software. All chemicals were of analytical grade and solutions were prepared with TraceSelect ultrapure water (Fluka).

During the Cooper field trial, the project team consistently measured anions at low parts-per-billion levels, as shown in the table. Figure 2 shows the analytical results for 1 and 50ppb concentrations of bromide, chloride, sulphate, nitrate, phosphate and fluoride. These species are of great interest to BWR operators due to their impacts on conductivity, stress corrosion cracking, and fuel performance. The

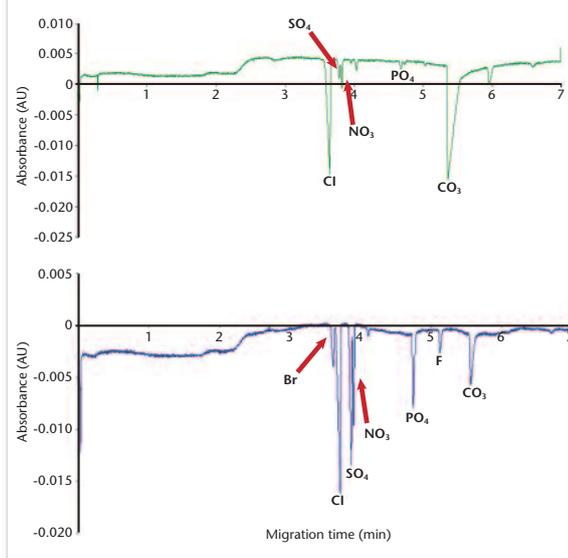
distinct absorbance spikes shown in Figure 2 illustrate the sensitivity of the CE technique at low levels.

In a second plant test, researchers used the CE method as a full-fledged analytical technique at Progress Energy's Brunswick Nuclear Plant. The project team used CE equipment to measure and determine the source of sulphate impurities detected in post condensate treatment process water samples. CE analysis determined that the source of the sulphates was organic and did not come from the resin beds, enabling the utility to keep a condensate bed in service. This rapid analysis saved the utility significant time and resulted in the discovery of a previously undetected plant condition that could be effectively resolved [5].

Additional research in 2007 and 2008 involved cation analysis for BWRs. In view of the success of squaric acid as a probe for anion analysis by CE, derivative cationic organic bases were synthesized to take advantage of the high UV absorptivity of the highly conjugated squarate group. This research evaluated two of the most promising squarate compounds: the single-charged cation referred to as P+, 3-(2-dimethylamino)-ethylamino-4-ethoxycyclobut-3-ene-1,2-dione, and the double-charged cation referred to as P++, 3,4-Bis-2-dimethylaminoethylamino-cyclobut-3-ene-1,2-dione, along with 4-(dimethyl amino)pyridine, known as DMAP, an aromatic compound that has been successfully used to determine low concentrations of selected cations in earlier work.

Experiments suggest that the DMAP probe is more effective for cation analysis via CE. The limits of detection for the cations of interest under optimised conditions are currently 10ppb in the laboratory – where baseline water purity unfortunately does not approach nuclear power plant standards. Figure 3 shows electropherograms of the cation analysis reproducibility for potassium, magnesium, sodium, calcium and lithium, all cations of interest for BWRs. A 2009 EPRI report documents this work. [6] Further research into cation analysis by CE is needed to demonstrate lower detection limits in operating plant environments, similar to those achieved for anion analysis.

Figure 2: Anion analysis of Br, Cl, SO₄, NO₃, PO₄ and F ions at concentrations of 1ppb (LEFT/TOP) and 50ppb (RIGHT/BOTTOM)



The Cooper and Brunswick demonstrations confirmed that CE can be a useful tool for detecting ionic species at very low concentrations. The performance of the equipment and the technique were considered a success by both its developers and utility chemistry personnel.

The demonstrations also showed that CE has the ability to track plant chemistry transient conditions rapidly and precisely. EPRI has been working with a commercial supplier of CE equipment to develop a fully automated system that will provide real-time CE analysis when installed on a plant's process streams. EPRI plans to demonstrate the online analysis capability at a BWR site in the future. ■

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