

Ion Analysis with Agilent Capillary Electrophoresis Systems

Application Compendium

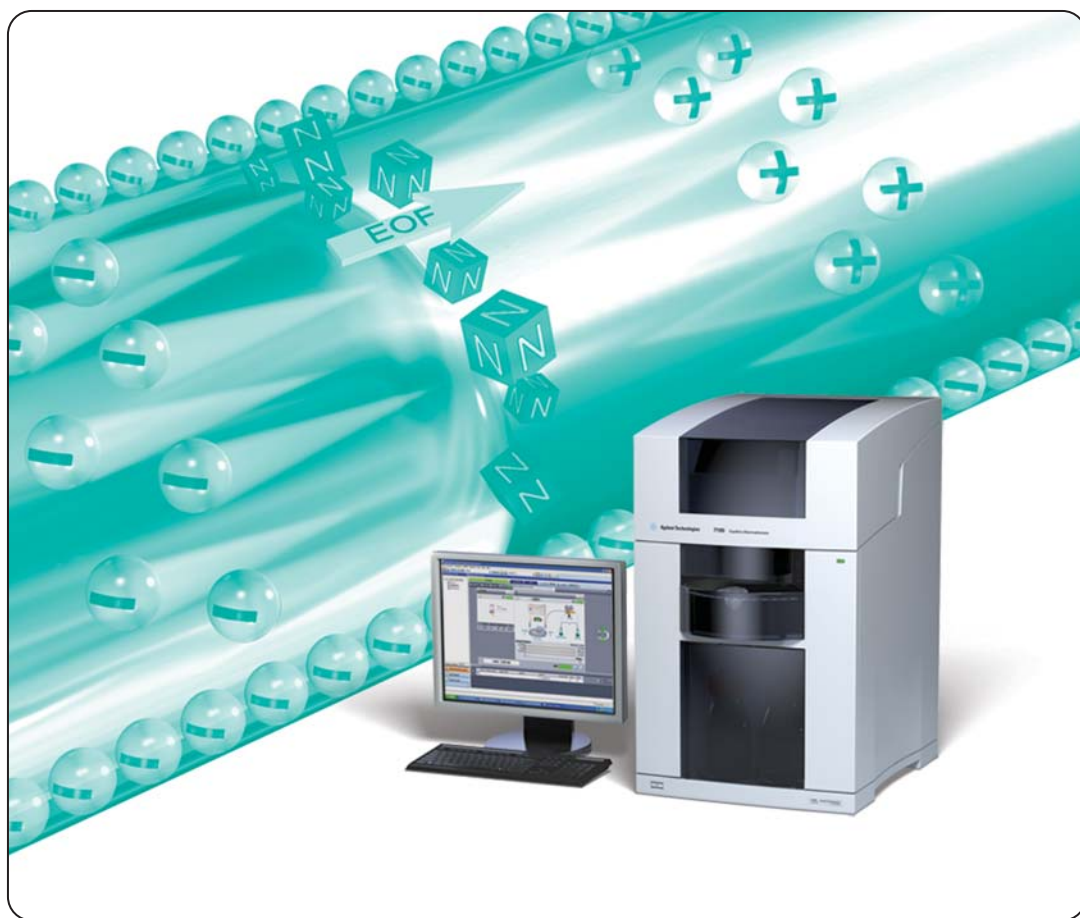


Table of Contents

Introduction	3
Determination of small ions by Capillary Zone Electrophoresis with indirect photometric detection	5
Cation Solution Kit for the Agilent 7100 Capillary Electrophoresis System	7
Inorganic Anion Analysis Kit for the Agilent 7100 Capillary Electrophoresis System	9
Organic Acid Solution Kit for the Agilent 7100 Capillary Electrophoresis System	11
Forensic Anion Solution Kit for the Agilent 7100 Capillary Electrophoresis System	13
Analysis of anions in power plant waters using Capillary Electrophoresis	15
Trace anion determination in semiconductor grade H ₂ O ₂ by Capillary Electrophoresis	17
Analysis of sulfur anions in Kraft liquors using Capillary Electrophoresis	19
Analysis of anionic contamination on wafer surfaces	21
ASTM standard: Recommended operating conditions for the Agilent Capillary Electrophoresis System	23
Monitoring of electroless plating baths by Capillary Electrophoresis	25

Introduction

Capillary Electrophoresis and the Agilent 7100 CE System

Capillary Electrophoresis (CE) offers fast separations with exceptional efficiency and resolution for charged substances such as biomolecules, low molecular weight basic or acidic drugs and ions – separations that are often difficult to achieve with HPLC.

CE also excels where sample amounts are very limited and requires clearly less buffer than liquid or ion chromatography. Used in standalone mode, as the separations component of a CE/MS or as a complementary, orthogonal technology to LC, the Agilent 7100 CE system brings unprecedented HPLC-like sensitivity to a wide range of analytical challenges.

- **Most sensitive CE on market**

Up to 10 x more sensitive than other CE instruments, featuring Extended Light Path Capillaries and High Sensitivity Cell

- **Widest choice of detectors**

The broadest detector portfolio including UV diode-array detector (DAD), mass spectrometry (MS), laser induced fluorescence (LIF), contactless conductivity detection (CCD) and other external detectors

- **Ready to use kits and methods or quick method development**

Complete kits, for example, for cations, anions or organic acids including robust methods allow for a jump start in Ion analysis. Easy parameter setup and test using CE-ChemStation with graphical user interface supports own method development

- **Only vendor offering replenishment system**

Reproducible throughput and exceptional linearity by unattended exchange of used buffers with fresh ones while minimizing number of buffer vials

- **Only vendor for complete CE-ESI-MS systems**

Complete CE-MS portfolio for Electrospray systems (Single-Quad, Triple-Quad, Time-of-Flight (TOF) and Q-TOF)



This Application Compendium describes the special criteria necessary for the separation and detection of small non-UV absorbing anions and cations. A number of applications are used to demonstrate the techniques.

Introduction to ion analysis

Separation of small ions is traditionally performed by ion-exchange chromatography using conductivity detection. This technique, known as ion chromatography (IC), has been successfully employed for decades. However, the technology has some limitations. Expensive and sometimes short-lived columns are required and the mobile phase is usually strongly acid or base. Pumping systems may require frequent maintenance for peak performance. Matrix effects are commonplace and extensive sample preparation may be required. The cost per analysis can be high. Capillary zone electrophoresis (CZE) is well suited for separating these species.

The basis for separation is the differences in mobilities among the various ions. This is readily exploited to perform high speed separations with superior speed and resolution compared with IC. The column required for ion-exchange chromatography, which can cost several hundreds of U.S. dollars can be replaced with a fused-silica capillary costing only a few dollars. Like most CZE methods, the cost per analysis is considerably less than comparable chromatographic methods. The problem here is detection. Most small ions do not absorb in the ultraviolet (UV) or visible regions of the spectrum.

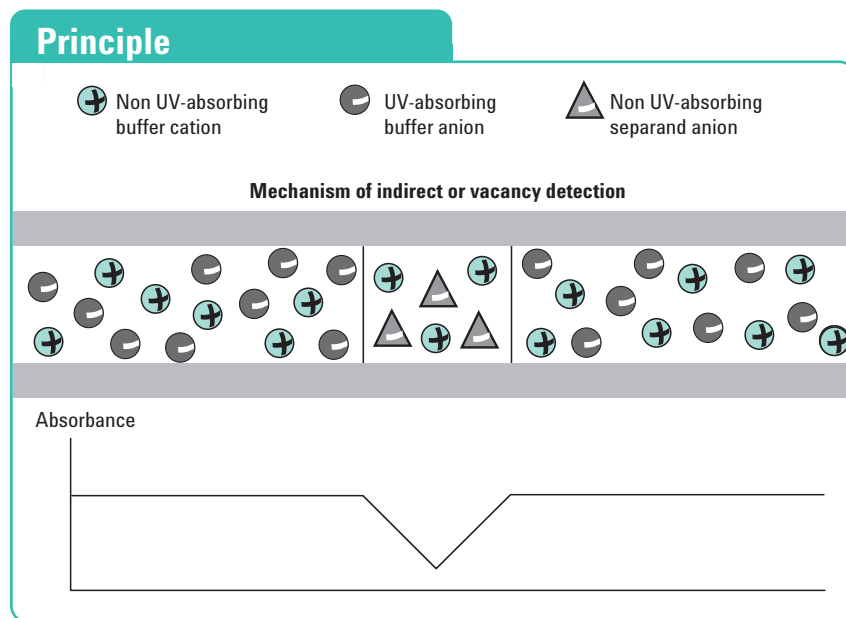


Figure 1
The principle of indirect photometric detection.

The detection problem is solved with indirect photometric detection (IPD), the principle of which is illustrated in figure 1. In this technique, a UV-absorbing solute of the same charge as the separands (a co-ion) serves as an additive to the background electrolyte (BGE). This additive, known as a visualizing reagent (VR) elevates the baseline. When solute ions are present, they displace the visualizing reagent as required by the principle of electroneutrality. As the separated ions migrate past the detector window, they are measured as negative peaks relative to the high baseline. By reversing the signal and reference wavelengths of the diode-array detector (DAD), a positive signal is obtained. With the spectral capability of the DAD, it is simple to select the optimal wavelengths for the reference and signal channels. It should be noted that CZE-IPD is suitable for virtually all ionic analytes lacking chromophores.

Alternative detection by CCD

Another option for detection is using a commercial contactless conductivity detector (CCD). Such a device can be added easily to the Agilent 7100 CE system since the required analog/digital converter is included and the temperature control by air supports direct installation of the detector within a standard capillary cassette.

Determination of small ions by Capillary Zone Electrophoresis with indirect photometric detection

Abstract

Fast and reliable analysis of cations is a request in various industries and applications. Food analysis is a widespread field with a large range of compounds and matrices to be handled. While in drinking water matrix effects are mostly neglectable other samples can be challenging. Capillary Electrophoresis is well suited for complex samples since the fused silica capillaries can be washed quick and thoroughly after each run allowing minimizing sample prep to a level that would not be acceptable to other techniques like chromatographic based separations.

Experimental and Results

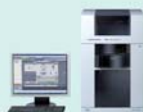
All experiments were performed using an Agilent Capillary Electrophoresis system equipped with a diode-array detector. An Agilent CE ChemStation was used for system control, data acquisition and post-run processing. All standards were reagent-grade materials. Buffer components were of the highest available purity. All buffer solutions were filtered through 0.2 μm -filters before use. Samples of yogurt, and mineral water were of German origin.

A variety of visualizing reagents (VRs) can be employed for indirect detection. In figure 1, a comparison is made between 5 mM imidazole and 5 mM p-aminopyridine (PAP) for detection of cations. For the highly mobile potassium and sodium ions, imidazole gives sharper peaks but for the less mobile ions, PAP is superior. The lower mobility of PAP is better matched to the mobilities of the slower migrating ions.

Conditions

Capillary: 75 μm id, L= 64.5 cm,
l = 56 cm
Field strength: +465 V/cm
Temperature: 35 °C
Detector: Signal 240 nm,
reference: 210 nm
Bandwidth: 10 nm

Agilent 7100 CE verified



Data measured with an Agilent 1600 CE system. Application verified with the Agilent 7100 Capillary Electrophoresis system, showing comparable or even better results.

Results

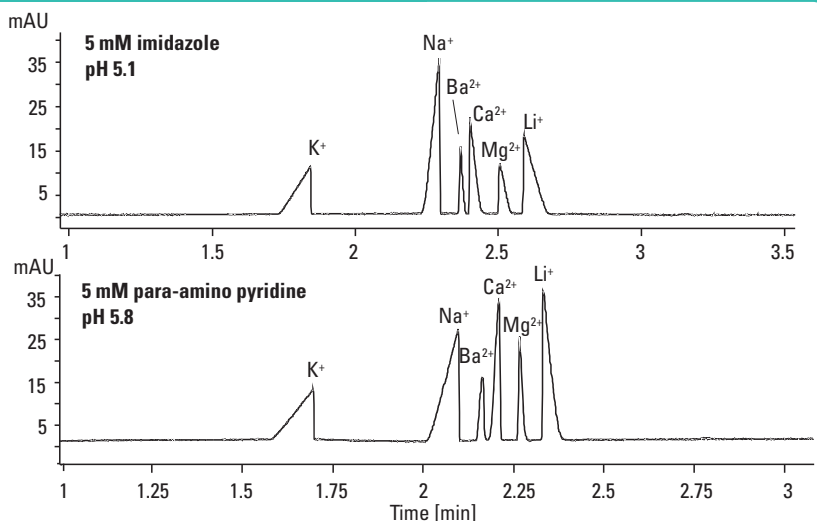


Figure 1
Separation of metal cations using 5 mM imidazole, pH 5.1 or 5 mM p-aminopyridine, pH 5.8 as visualizing agents.

Applying this chemistry to the determination of cations in a 100-fold aqueous dilution of yogurt (figure 2a), and mineral water (figure 2b) provided some interesting data. In figure 2b, the signals for sodium, calcium and magnesium corresponded to 1.2, 1.2 and 0.3 ppm respectively in the diluted sample. For magnesium, the estimated LOD was 30 ppb. A 100-fold aqueous dilution provided an effective stacking medium. Note in particular, the peak width of the potassium ion. The broadened peak in red wine is indicative of the high potassium level. This mobility mismatch is always amplified at high solute concentration. However, since resolution is superior, quantitation will be accurate as long as peak areas are used. If sharpening of the potassium peak is desired, a higher mobility VR will have to be selected. Alternatively, the mobility of potassium can be reduced using a crown ether. Using mobility matching techniques, it is possible to sharpen any peak of interest.

Results

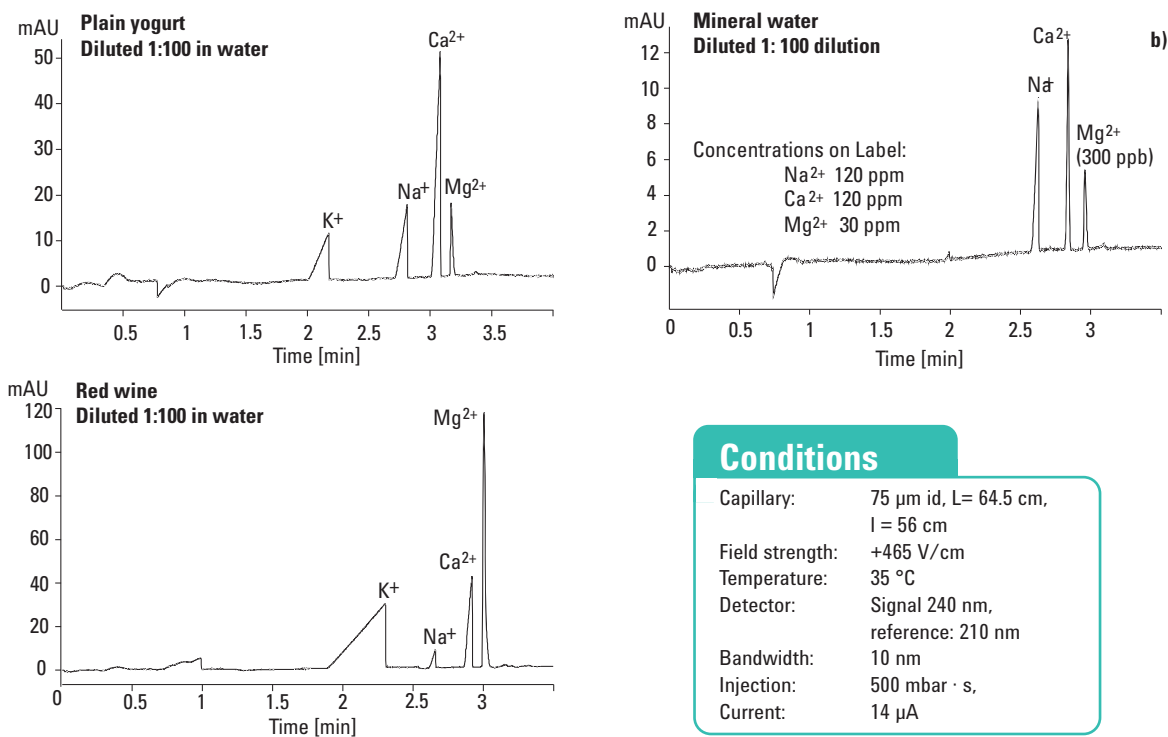


Figure 2
Separation of metal cations in yogurt, mineral water and red wine.

Cation Solution Kit for the Agilent 7100 Capillary Electrophoresis System

Introduction

The performance of the Agilent 7100 Capillary Electrophoresis system using the Cation Solution kit is described here. This kit contains necessary supplies for the separation of cations. The kit permits the analysis of cations in indirect UV detection mode. It is also suitable for the separation of low-molecular weight amines. The cation buffer and all other reagents provided in this kit are ready-to-use. A complete cation analysis CE method with statistical analysis on migration time is described.

Experimental and results

Cation analysis was performed using the Agilent 7100 CE system equipped with DAD detection using 56-cm effective length capillary. The method is based on the Agilent Cation Solutions Kit (PN 5064-8206).

- The buffer should be replaced every second run when using 1 mL polypropylene vials, since the buffer used for indirect UV detection has limited buffering capacity.
- The buffer should be stored at 4 °C.
- The Cation Test Mixture stock should be stored at 4 °C. Prior to use, the test sample should be diluted 1:10 with CE grade water.
- Prior to first use, a new capillary should be conditioned with run buffer for 15 minutes.
- Between analyses, it is recommended that the capillary is flushed with run buffer (2 min) from the flush vial.

Analysis of the Cation Test mixture

The electropherogram in figure 1 shows a typical separation of the Cation Test sample (1:10 dilution) demonstrating the performance of the Agilent 7100 CE system. The mixture of five – cations was well resolved within 5 minutes.

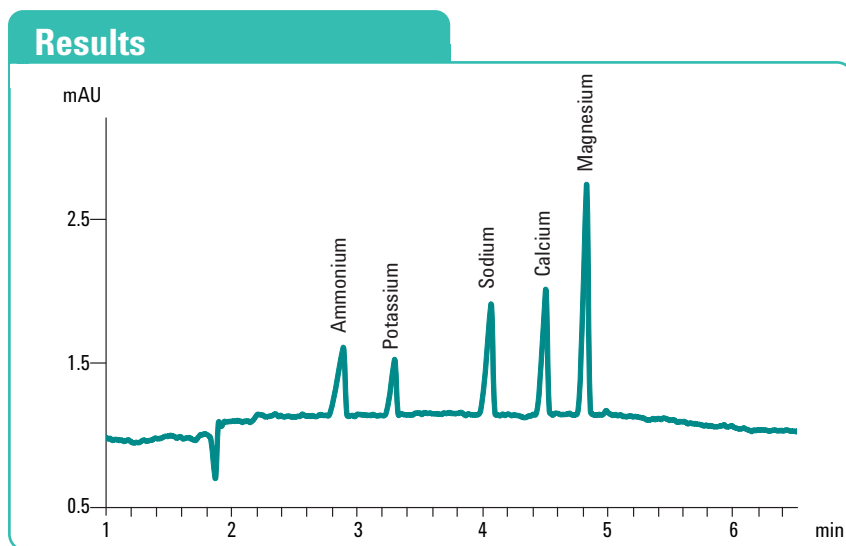


Figure 2
Electropherogram of Cation Standard.

Migration time and peak area reproducibility is highly dependent on the use of fresh buffer and capillary conditioning. The 7100 CE software allows to easily program and reuse conditioning methods to customize and automate any required procedures. Figure 2 provides data on observable differences in CV of migration times for changed run temperatures. In general changes of ± 1 °C did not show a significant effect on migration time reproducibility (n = 5) . The coefficients of variations of migration time were all less than 1 %. The results are comparable to those using the earlier Agilent 1600 CE system.

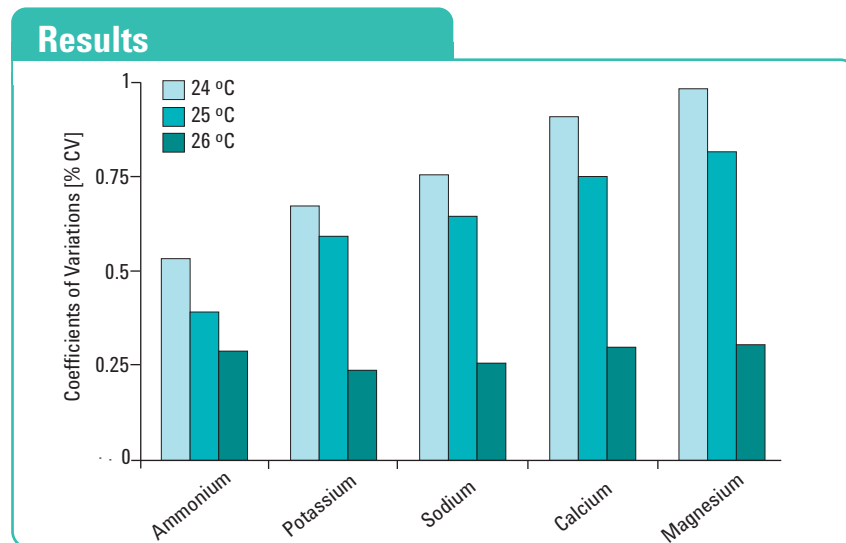


Figure 2
Effect of temperature on migration time reproducibility (n=5).*

Tap water analysis

Monitoring of cations is important for the classification of drinking water. We analyzed absolute values of tap-water using the Agilent Cation Solutions kit. Peak identification was performed via migration time comparison with the Cation Test sample. The % CV values for migration time were less than 0.9 % as shown in figure 3.

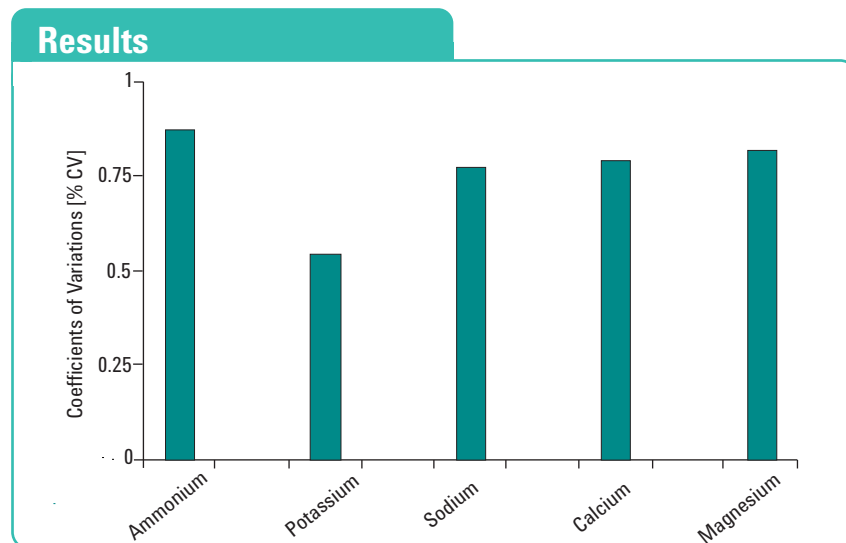


Figure 3
Migration-time reproducibility for CE analysis of tap water (n=5).*

* Raw data are used to plot the data. No internal standard is considered for calculations.

Inorganic Anion Analysis Kit for the Agilent 7100 Capillary Electrophoresis System

Introduction

The performance of the Agilent 7100 Capillary Electrophoresis system using the Inorganic Anion Analysis kit is described here. With this kit inorganic anions in indirect UV detection mode can be analyzed. The electrophoresis is carried out in reverse polarity since the EOF is reversed. The anion buffer and all reagents provided in the kit are ready-to-use. A complete inorganic anion analysis CE method including data on migration time reproducibility is described.

Experimental and results

Inorganic anion analysis was performed using the Agilent 7100 CE system equipped with DAD detection using a 72-cm effective length capillary. The method is based on the Agilent Inorganic Anion Analysis kit (PN 5063-6511).

- The buffer should be replaced every five runs when using 2 mL glass vials, since the buffer used for indirect UV detection has limited buffering capacity.
- The buffer should be stored at 4 °C.
- The Inorganic Anion Test Mixture stock should be stored at 4 °C. Prior to use, the test mixture should be diluted 1:100 with CE grade water.
- Prior to first use, a new capillary should be conditioned with 1 N NaOH (10 min), CE grade water (10 min) and run buffer (30 min).
- Between analyses, it is recommended to flush the capillary with 0.1 N NaOH (3 min) and run buffer (5 min).

Analysis of Inorganic Anion Test Mixture

The electropherogram in figure 1 shows a typical separation of the Inorganic Anion Test Mixture, included in the kit. This demonstrates the typical performance of the Agilent 7100 CE system. The mixture of six anions was well resolved in 9 minutes.

Migration time and peak area reproducibility is highly dependent on the use of fresh buffer and also capillary conditioning. The Agilent 7100 CE software allows

Results

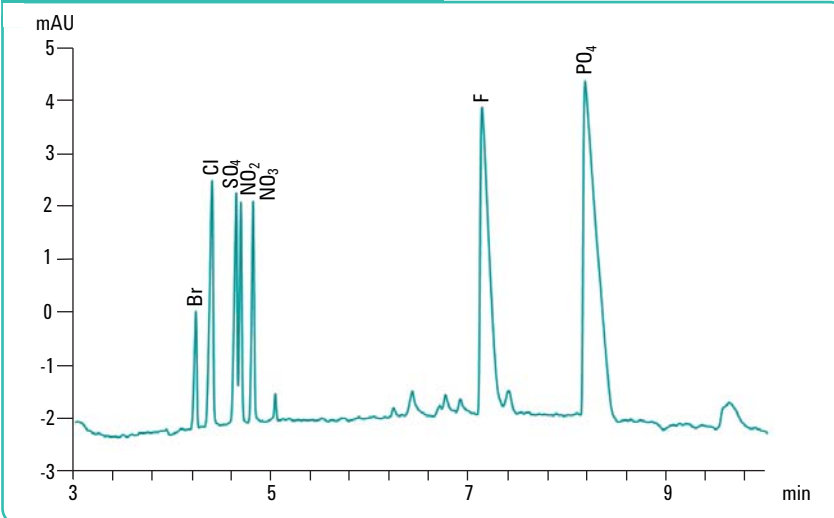


Figure 1
Electropherogram of Inorganic Anion Standard.

to easily program and reuse conditioning methods to customize and automate any required procedures. Differences in run temperature ($\pm 1^\circ\text{C}$) did not show a significant effect on migration time values in figure 2 ($n = 5$). The coefficients of variations of migration time were less than 2.4 %. The results are comparable to those using the earlier Agilent 1600 CE system.

Results

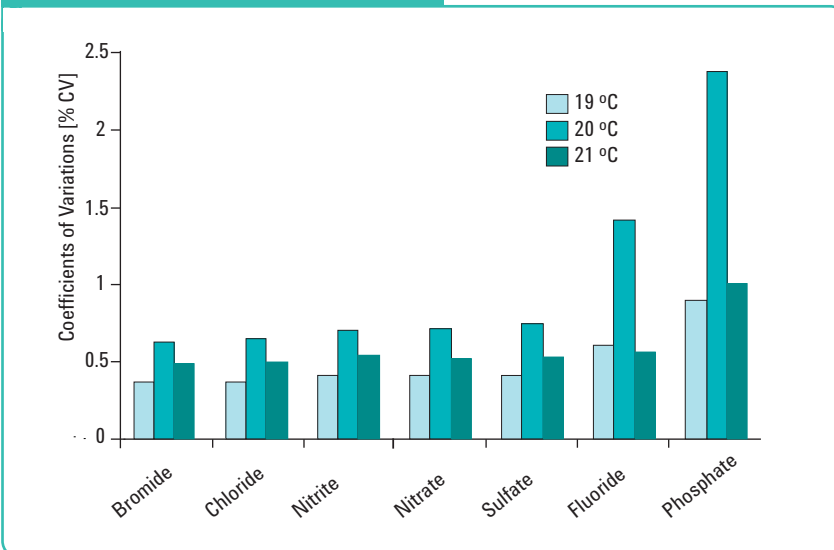


Figure 2
Effect of temperature on migration time reproducibility ($n=5$).
Raw data are used to plot the data. No internal standard is considered for calculations.

Organic Acid Solution Kit for the Agilent 7100 Capillary Electrophoresis System

Introduction

The performance of the Agilent 7100 Capillary Electrophoresis system using the Organic Acid Solution kit is described here. This kit was developed to facilitate the analysis of common organic acids and some inorganic anions. Since most of these compounds do not absorb significantly in the UV, detection is performed indirectly. The organic acid buffer and all other reagents provided in this kit are ready-to-use. A complete organic acid analysis CE method including data on migration time reproducibility is described.

Experimental and results

Organic acid analysis was performed using the Agilent 7100 CE system using 72-cm effective length capillary. An indirect UV detection agent optimized for organic acids was used. The method is based on the Agilent Organic Acids Solution kit (PN 5063-6510).

- The buffer should be replaced every five runs when using 2 mL glass vials, since the buffer used for indirect UV detection has limited buffering capacity.
- The buffer should be stored at room temperature.
- The Organic Acid Test Mixture stock should be stored at 4 °C. Prior to use, the test mixture should be diluted 1:40 with CE grade water.
- Prior to first use, a new capillary should be conditioned with run buffer for 15 minutes.
- Between analyses, it is recommended that the capillary is flushed with run buffer for 4 minutes.

Organic acid analysis

The Organic Acid Solution kit is ideal for the analysis of short alkyl chain carboxylic acids. The electropherogram in figure 1 shows a typical separation of the Organic Acid Test mixture, included in the kit, demonstrating the performance of the Agilent 7100 CE system. The mixture of three organic acids was well resolved in 7 minutes.

Results

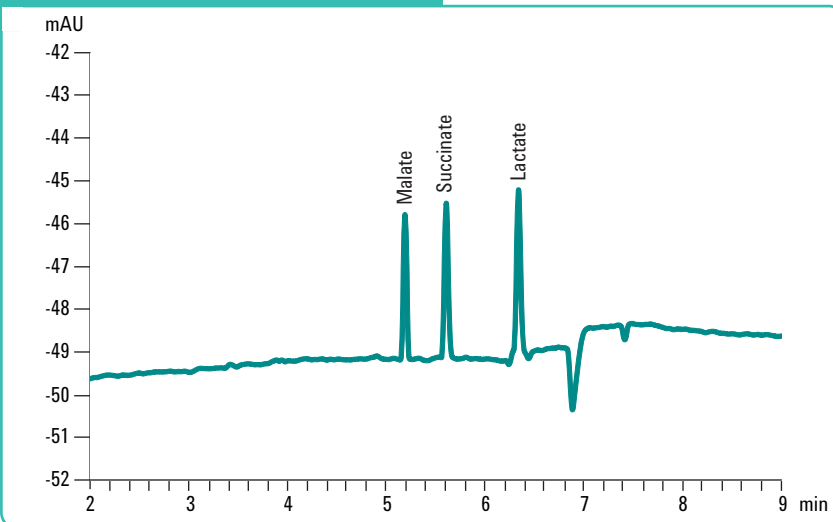


Figure 1
Electropherogram of Organic Acids Test Mixture (1:40 diluted with CE grade water).

Migration time and peak area reproducibility is highly dependent on the use of fresh buffer and also capillary conditioning. The Agilent 7100 CE software allows to easily program and reuse conditioning methods to customize and automate any required procedures. Figure 2 provides data on observable differences in CV of migration times for changed run temperatures. Differences in run temperature ($\pm 1^\circ\text{C}$) didn't show a significant effect on migration time reproducibility ($n = 5$). The coefficients of variations of migration time were all less than 0.13 %. The results are comparable to those achieved using the earlier Agilent 1600 CE system.

Results

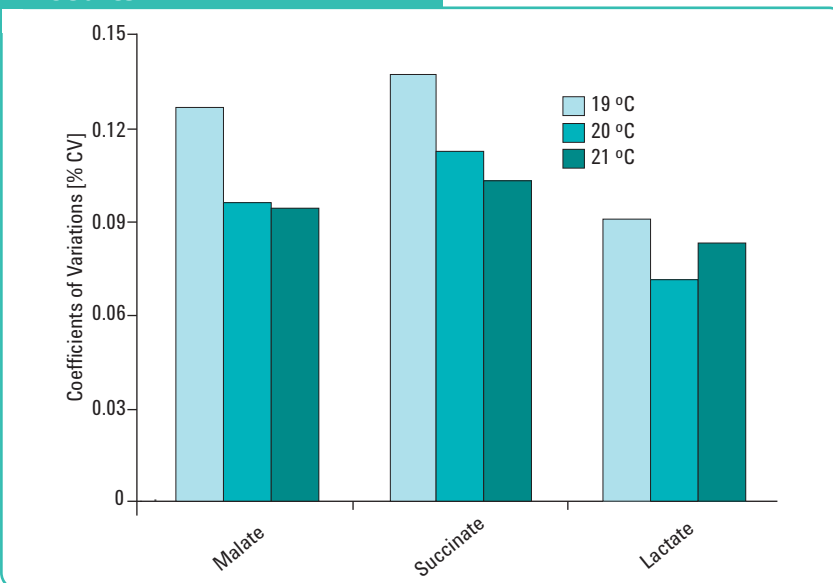


Figure 2
Effect of temperature on migration time reproducibility ($n=5$).
Raw data are used to plot the data. No internal standard is considered for calculations.

Forensic Anion Solution Kit for the Agilent 7100 Capillary Electrophoresis System

Introduction

The performance of the Agilent 7100 Capillary Electrophoresis system using the Forensic Anion Solution kit is described here. This kit contains the supplies necessary for the separation of inorganic anions. The kit facilitates the analysis of anions in indirect UV detection mode. The buffer and all other reagents provided in this kit are ready-to-use. A complete anion analysis CE method including data on migration time reproducibility is described.

Experimental and results

Inorganic anion analysis was performed using the Agilent 7100 CE system equipped with DAD detection using a 104-cm effective length capillary. The method is based on the Agilent Forensic Anion Solution Kit (PN 5064-8208).

- The buffer should be replaced every ten runs when using 2 mL glass vials or every five to six runs when using 1 mL polypropylene vials, since the buffer used for indirect UV detection has limited buffering capacity.
- The basic anion buffer should be stored at room temperature (some buffer components may crystallize at lower temperatures) and be protected from CO₂ to prevent pH changes
- The Inorganic Anion Test Mixture stock should be stored at 4 °C. Prior to use, the test mixture should be diluted 1:10 with CE grade water.
- Prior to first use, a new capillary should be conditioned with run buffer (15 min).
- Between analyses, it is recommended that the capillary is flushed for 2 minutes with run buffer from the Outlet Home vial then for 2 minutes with run buffer from the Inlet Home vials.

Analysis of Inorganic Anion Test Mixture

To identify anionic toxins a quick and accurate analysis is required. The Forensic Anion Solutions kit is ideally suited for the analysis of such anions. The electropherogram in figure 1 shows the separation of the Inorganic Anion Test Mixture (1:10 dilution), demonstrating the performance of the Agilent 7100 CE system. The seven anions of the test mixture were well resolved within 9 minutes.

Results

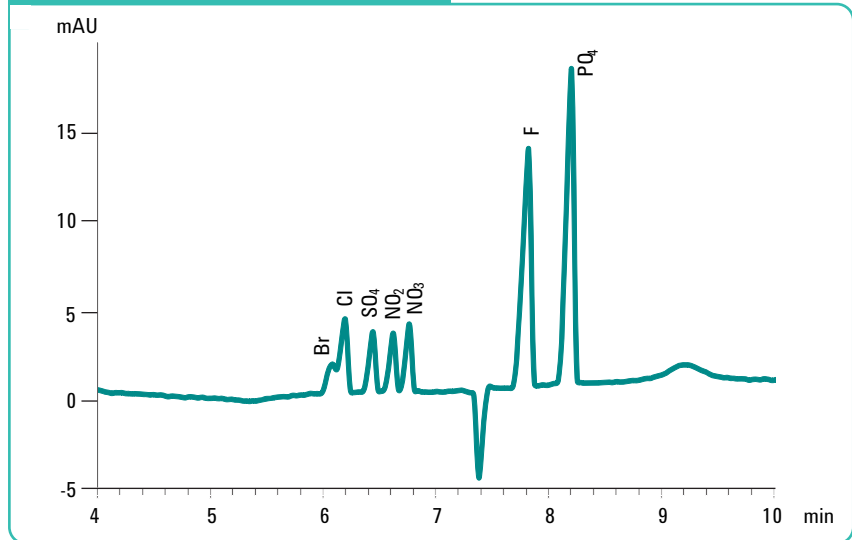


Figure 1
Electropherogram of 1:10 diluted Inorganic Anion Standard (phosphate 200 ppm, others 100 ppm each).

Migration time and peak area reproducibility is highly dependent on use of fresh buffers and also capillary conditioning. The 7100 CE software allows to easily program and reuse conditioning methods to customize and automate any required procedures. Figure 2 provides data on observable differences in CV of migration times for changed run temperatures. Differences in run temperature ($\pm 1^\circ\text{C}$) were analyzed too see the variation in migration time. The coefficients of variations of migration time were all less than 0.36 %. The results are comparable to those using the earlier Agilent 1600 CE system.

Results

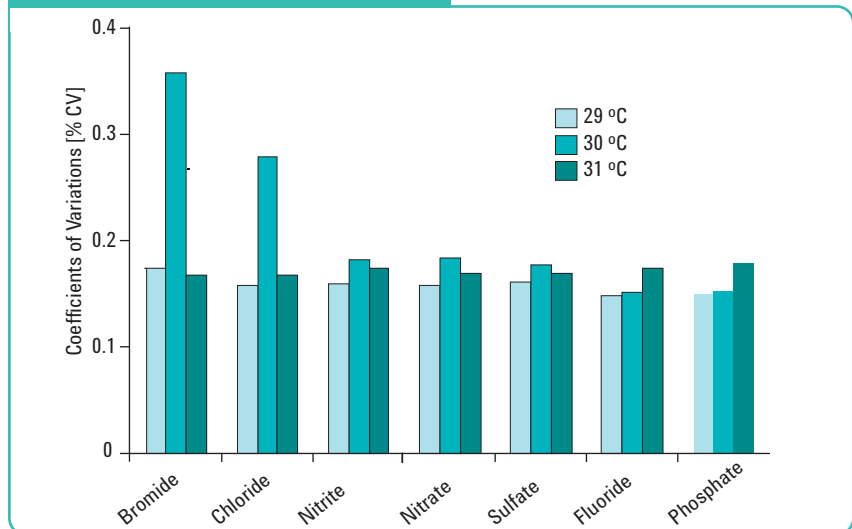


Figure 2
Effect of temperature on migration time reproducibility (n=5).

Raw data are used to plot the data. No internal standard is considered for calculations.

Analysis of anions in power plant waters using Capillary Electrophoresis

Abstract

Power plant circuit waters must be ultrapure and treated to minimize corrosion. Additives are ammonia and/or morpholine (pH control), and hydrazine (powerful reducing agent). Corrosion products, consisting mainly of insoluble metal species, build up deposits in the tubings where trace ionic contaminants from the feedwater can concentrate resulting in a highly corrosive local environment. Low levels of small anions and cations must therefore be monitored in order to minimize operational costs and contribute to the safe operation of the plant. Low ppb levels of small inorganic and organic anions are analyzed fast and reliably by capillary electrophoresis (CE) using indirect UV detection.

Experimental and results

Anion analysis was performed using the Agilent Capillary Electrophoresis system equipped with DAD detection and computer control via Agilent ChemStation. The method is based on the Agilent Inorganic Anion Solutions Kit (part number 5063-6511). A bubble cell capillary was used to increase detection limits. Additionally, the capillary effective length was reduced to 50 cm to shorten analysis times without sacrificing resolution between nitrate and oxalate. All vials (glass vials for buffer, polypropylene vials for samples) and clear olefine vial caps were washed overnight with deionized water (Milli-Q Plus or comparable quality) to eliminate contamination. Deionized water was also used to prepare the anion standards daily. Gluconic acid (10 mM) was added to all standards and samples to decrease carbonation.

New capillaries were subjected to a conditioning procedure: 10 minutes flush 1 N NaOH, 3 minutes flush 0.1 N NaOH, dip inlet/outlet in water, 15/30 minutes flush from two different buffer vials. Each flush step used its own waste vial. Afterwards, 10 standard runs injecting hydrodynamically from a 100 ppb standard solution in water were performed thereby equilibrating the capillary.

Prior to each analytical run a preconditioning procedure together with automatic buffer vial replenishment was performed to keep migration times stable. This procedure and more details are found in the caption of figure 1, which shows the analysis of anions in reconstituted secondary circuit water matrix. The assay was linear over the range 10–30 ppb ($r^2 > 0.98$) with a detection limit of 1-5 ppb. This was sufficient for reliable determination of ion concentrations normally found in circuit water samples. Repeatability ($n = 6$, with internal standard) was 0.08 - 0.19 % RSD for migration times and 2.68–5.63 % RSD for corrected peak areas (except for acetate, 10.44 % RSD). This excellent migration time repeatability was achieved even in the presence of a complex sample matrix. The repeatability of peak areas was sufficient for reliable quantitation.

Agilent 7100 CE verified



Data measured with an Agilent1600 CE system. Application verified with the Agilent 7100 Capillary Electrophoresis system, showing comparable or even better results.

Results

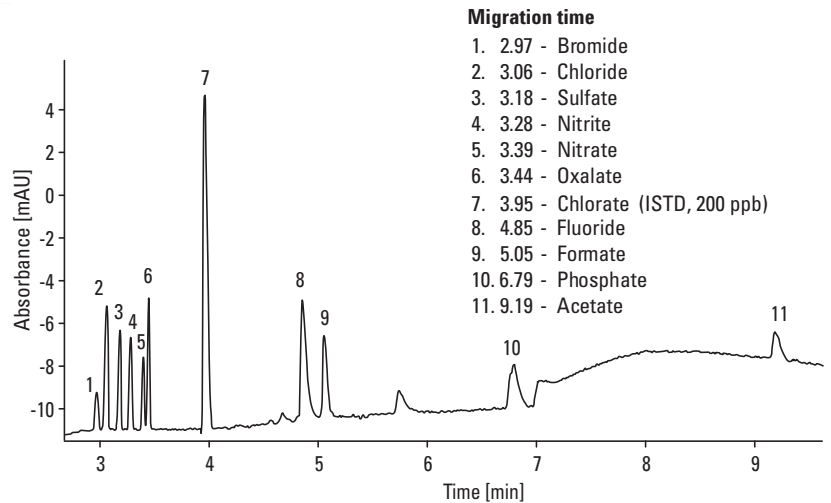


Figure 1
The analysis of anions in reconstituted secondary circuit water matrix.

Electrophoretic conditions

Sample:	20 ppb anions in matrix, (5 ppm morpholine, 50 ppb hydrazine, 300 ppb ammonia, 300 ppb methylamine, 5 ppm borate)
Injection:	-5 kV x 20 sec
Capillary:	Length = 58.5 cm, effective length = 50 cm; 50 µm id, BF3
Buffer:	Inorganic anion buffer
Temperature:	30 °C
Voltage:	30 k, negative polarity
Detection:	Signal 350/50, reference 245/10
Precondition:	Flush 2 min 0.1 N NaOH, dip both ends in water, flush 2 x 2 min with electrolyte

Trace anion determination in semiconductor grade H₂O₂ by Capillary Electrophoresis

Abstract

During VPD-TXRF measurements, a combination of vapor-phase decomposition (VPD) and total reflection x-ray fluorescence (TXRF), H₂O₂ is used as oxidizing reagent in order to collect cationic contamination on silicon wafer surfaces 1. VPD-TXRF detection limits strongly depend on the H₂O₂ purity. High sulfur levels as well as bromine and chlorine interfere with the analysis. Organic acids are also monitored. Semiconductor Equipment and Materials International (SEM) recommends a TOC (total organic carbon) concentration of 10 ppm in H₂O₂ used during the manufacturing of integrated circuits with structure width below 0.25 μm. This analysis is faster and easier to achieve with capillary electrophoresis than with the comparable ion chromatography method. Decomposition or dilution prior to the analysis is not necessary minimizing the probability of cross-contamination.

Experimental and results

All experiments were performed on an Agilent Capillary Electrophoresis system, and the Agilent Inorganic Anion Solutions kit (5063-6511). Sample preparation and analysis was carried out in a Class 5 (ISO 14644-1) flow box. Anion stock solutions (1000 ppm of the corresponding sodium salt) were prepared with ultra-pure water (according to the Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry ASTM D5127-99). Multi-anion calibration standards at the ppb level were prepared from single standards immediately before use. Prior to first use a new capillary was flushed for 2 minutes with water, 30 minutes with 500 mM NaOH, 5 minutes with water, and 30 minutes with electrolyte (at 1 bar, 40 °C). Then voltage conditioning was performed (10 minutes, - 30 kV, 20 °C). The capillary was subsequently equilibrated under separation conditions (50 μM anion standard, five analyses). The H₂O₂ was of the purest available grade (Ultra Large Scale Integrated circuits, ULSI). Given the large concentration range of analytes, three injection modes were applied: hydrodynamic injection (25 mbar · 10 sec), stacking (10 mM NaOH for 25 mbar · 5 sec, sample for 50 mbar · 95 sec), and electrokinetic injection (10 sec · -10 kV. For electrokinetic injection 300 μL sample was brought in a 1-mL polypropylene vial. Given this volume and a capillary offset of 4 mm, only the very end of the capillary and the tip of the electrode dip into the sample solution. The electrode material catalytically decomposes H₂O₂, and O₂ should not enter the capillary. For this reason only one injection per vial is recommended.

Agilent 7100 CE verified



Data measured with an Agilent 1600 CE system. Application verified with the Agilent 7100 Capillary Electrophoresis system, showing comparable or even better results.

Figure 1 shows the analysis of 30 % ULSI-hydrogen peroxide (table 1 for quantitative results). Unknown peaks are assumed to be organic components with no influence on the VPD-TXRF measurement. Migration time reproducibility (n = 5) for compounds > 5 ppb concentration was below 0.3 % RSD, and corrected area reproducibility was below 3 % RSD (except for tartrate, nitrate and formate, < 10 % RSD). The assay was linear over a range of 50–500 nM for electrokinetic injection (detection limit 10 nM), 0.5–10 μM for stacking, and 5–250 μM for hydrodynamic injection. Quantitation was based on standard addition (100 μL spiked standard added to 10 mL sample, 6 levels within the linear range per injection mode). Nitrite could not be properly quantified due to oxidation processes on the sample.

References

1. Book of SEMI Standards 0998, Materials Volume, SEMI M33-0998: "Test Method for the Determination of Residual Surface Contamination on Silicon Wafers by Means of Total Reflection X-Ray Fluorescence Spectroscopy (TXRF)"
2. Ehmman, T. et al, *J. Chromatogr. A* 816, 261-275, 1998.

Results

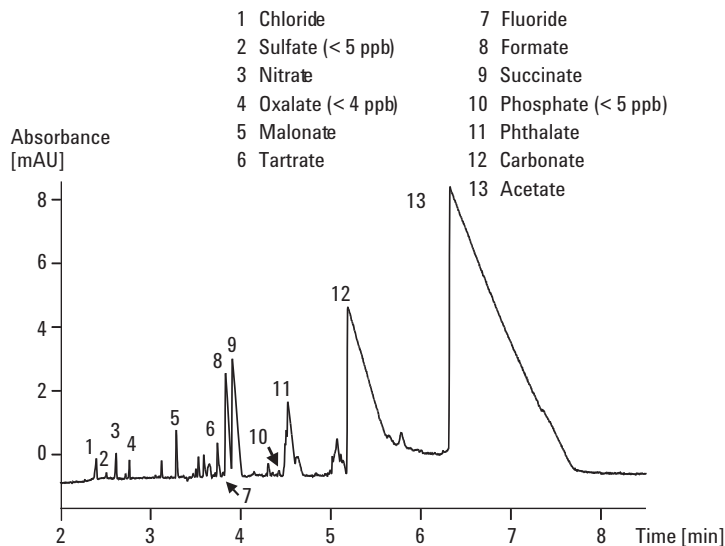


Figure 1
Analysis of anions in 30 % ULSI-H₂O₂.

Electrophoretic conditions

Sample: 30 % ULSI hydrogen peroxide
Injection: Electrokinetic: 10 sec · -10 kV
Capillary: L = 48.5 cm, l = 40 cm, 50 μm id
Buffer: Inorganic Anion Buffer (PN 8500-6797)
Voltage: -30 kV
Temperature: 20°C
Detection: Signal 350/60 nm, reference 245/10 nm
Preconditioning: Flush with 0.25 M propionic acid for 0.5 minutes, flush with buffer for 3 minute²

Anion	Concentration [ppb]	r ²	Linear equation	Injection mode
Chloride	12	0.9996	y = 0.00227 x + 0.7435	Electrokinetic
Nitrate	16	0.9989	y = 0.002563 x + 0.6446	Electrokinetic
Malonate	55	0.9995	y = 0.002885 x + 1.3255	Electrokinetic
Tartrate	36	0.9999	y = 0.004717 x + 1.1438	Electrokinetic
Fluoride	2	0.9990	y = 0.002633 + 0.2999	Electrokinetic
Formate	203	0.9996	y = 0.5679 x + 2.5598	Stacking
Succinate	721	0.9997	y = 1.1103 x + 6.9003	Stacking
Phthalate	966	0.9997	y = 0.0205 x + 0.00350	Stacking
Acetate	14859	0.9997	y = 0.000125 x + 0.03158	Hydrodynamic

Table 1
Quantitative results for the analysis of of 30 % ULSI-hydrogen peroxide.

Analysis of sulfur anions in Kraft liquors using Capillary Electrophoresis

Abstract

The proper function of Kraft recovery furnaces is a very important part of the chemical recovery process at a Kraft pulp mill. In the recovery furnace sulfur anions, such as sulfate in the black liquor are converted to sulfide anions in the green liquor. Sulfide anions in the pulping reactions produce stronger paper and if its concentration is too low, the paper produced loses its strength. If the sulfide concentration is very high, polluting emissions from the Kraft recovery furnaces are increased. Wet chemical tests and ion chromatography (IC) have traditionally been used to analyze process liquors. CE is a worthy replacement for IC due to less buffer consumption, less maintenance, and considerably shorter run times.

Experimental and results

In the pulp and paper industry Kraft liquors must be monitored for the anion content both to monitor the quality of the liquors and for environmental reasons. CE is used to measure sulfur anions (sulfide, sulfate, thiosulfate and sulfite), chloride anions and oxalate anions. Wet chemical tests are used for hydroxide, carbonate, sulfide and sulfate anions. The sulfate and sulfide anions are used to calculate the percent reduction of the green and white liquor, which is one measure of the efficiency of the recovery furnace. Control personnel uses the results of the tests to adjust process control parameters that influence the degree of conversion of sulfur containing anions to sulfide anions.

CE is also used to measure the amount of chloride ions in Kraft recovery process liquors. Chloride concentrations tend to build up in the recovery process to an equilibrium level depending on inputs to the system. High chloride concentration can be detrimental because it increases the rate of corrosion for some type of metals.

Anion analysis was performed using the Agilent Capillary Electrophoresis system equipped with diode array detection and computer control via the Agilent ChemStation. The chemical method is based on the Agilent Inorganic Anion kit. The pH of the buffer is raised to make sulfur species stable (for details see conditions next to figure). Migration times were stabilized by flushing the capillary with sodium hydroxide and buffer and replenishing buffer vials prior to each run. Available modification to the Agilent CE system provides for blanketing the replenishment system with helium to prevent oxidation of sulfide and sulfite anions. All standards (10,000 ppm sulfide, sulfate, Cl) were prepared in 0.1 N NaOH. Sample preparation consisted simply of diluting the sample 1:200 with water.

Agilent 7100 CE verified



Data measured with an Agilent 1600 CE system. Application verified with the Agilent 7100 Capillary Electrophoresis system, showing comparable or even better results.

The assay was linear over the range 10 to 100 ppm with an $r^2 = 0.99997$. The detection limit in the Kraft liquors was approximately 1 ppm. Samples containing 20 g/L sulfide and 1 g/L of the other components could be routinely analyzed.

Results

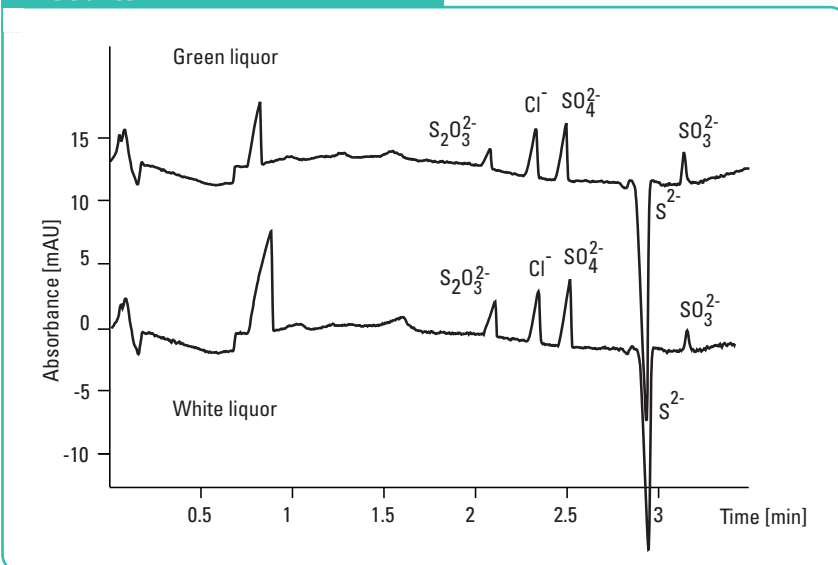


Figure 1
Analysis of green and white Kraft liquors.

Electrophoretic conditions

Sample: Green and white Kraft liquor
Injection: 1 sec @ 50 mbar sample, dip inlet in water, 2 sec @ 50 mbar buffer
Capillary: Effective length 24.5 cm, total length 33 cm, internal diameter 50 μm
Buffer: 2.25 mM pyromellitic acid, 6.5 mM sodium hydroxide, 0.75 mM hexamethonium hydroxide, 1.6 mM triethanolamine, pH 11.2
Voltage: -18 kV
Temperature: 35 $^{\circ}\text{C}$
Detection: Signal 350/50 nm, reference 235/10 nm
Preconditioning: 2 min flush with 0.1 N NaOH, 4.2 min flush with buffer, at 1 bar each

Analysis of anionic contamination on wafer surfaces

Abstract

The quality of a wafer can be seriously affected by ionic impurities on its surface. As part of quality control programs in most semiconductor facilities, anions, cations, metals and amines are routinely measured to determine the level of contamination. Anionic impurities have increasingly attracted attention because they lead to additional etching of the oxide layer, causing light-point defects and affecting the amount of metals that adhere to the wafer surface. Low sample consumption and cost per analysis together with high speed and short turnover times make capillary electrophoresis (CE) very suitable for the analysis of low ppb levels of anions on wafer surfaces.

Experimental and results

Anion analysis was performed on a Agilent Capillary Electrophoresis system equipped with diode array detector and controlled through a PC-based Agilent ChemStation. The analysis was based on the Agilent inorganic anion analysis kit (see figure caption for more details). All vials (glass vials for buffer, polypropylene vials for samples) and clear polyurethane caps were washed with ultrapure water (UPW) which fulfilled the requirements of the SEMI guidelines. Anion stock solutions and electrolyte were prepared in a class 10,000 flow box. Calibration standards were prepared daily immediately before use in a clean room under a class 10 laminar flow hood.

Prior to first use new capillaries were treated by a 30 min flush with 0.5 M NaOH, a 30 min flush with electrolyte, and 60 min conditioning at -30 kV. A capillary was considered to be equilibrated when migration time repeatability of 5 consecutive runs using hydrodynamic injection was < 2% RSD.

Agilent 7100 CE verified



Data measured with an Agilent 1600 CE system. Application verified with the Agilent 7100 Capillary Electrophoresis system, showing comparable or even better results.

A typical electropherogram of the analysis is shown in figure 1. Repeatability ($n = 20$, with internal standard) was < 0.5% RSD for migration times and < 3% RSD for corrected peak areas. Table 1 shows linear ranges and detection limits of the assay using electrokinetic injection. Linearity ranges given are based on correlation coefficients $r^2 > 0.996$.

The data obtained here correlated well with results from ion chromatography (IC). However, CE is more suitable in terms of cost per analysis and ease of use.

References

Ehmann et al., "Optimization of the Electrokinetic Sample Introduction in Capillary Electrophoresis for the Ultra Trace Determination of Anions on Silicon Wafer Surfaces", *Chromatographia* (1997), Vol. 45, 301–311 (available as Agilent publication number 5966-1991E)

Results

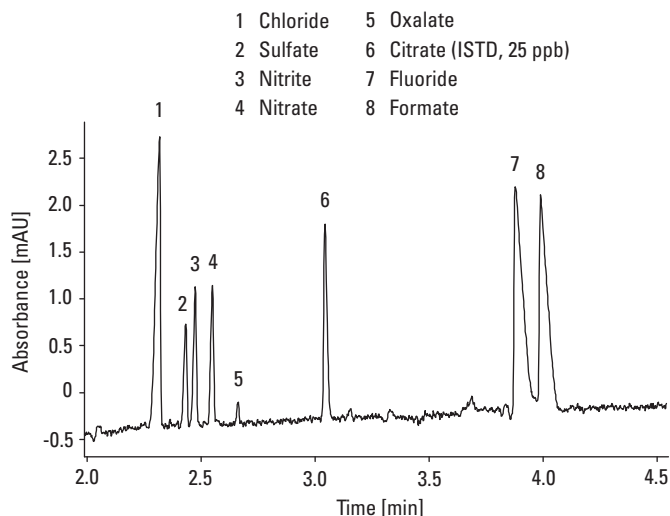


Figure 1
Analysis of anions on wafer surfaces by capillary electrophoresis.

Electrophoretic conditions

Sample: 500 μ l out of 3 mL ultrapurewater used for complete wetting of a 200 mm wafer
Injection: 125 mbar \cdot s 10 mL NaOH, 5 s water dip followed by -10 kV \times 10 s sample injection
Capillary: Effective length 40 cm, total length 48.5 cm, internal diameter 50 μ m
Buffer: 2.25 mM pyromellitic acid, 6.5 mM sodium hydroxide, 0.75 mM hexamethonium-Hydroxide, 1.6 mM triethanolamine, pH 7.7, buffer replenishment prior to each run
Voltage: 30 kV, negative polarity
Temperature: 20 $^{\circ}$ C
Detection: Signal 350/60 nm, reference 245/10 nm
Preconditioning: Flush with 0.25 M, HCl for 0.5 min, flush with buffer for 3 min prior to each run

Anion	Linear Range (ppb)	Detection Limit (ppb)
Bromide	4–40	0.8 \pm 0.5
Chloride	2–18	0.4 \pm 0.2
Sulfate	5–48	1.0 \pm 0.2
Nitrite	2–23	0.5 \pm 0.3
Nitrate	3–31	0.6 \pm 0.4
Oxalate	4–44	0.9 \pm 0.2
Chlorate	4–42	0.8 \pm 0.6
Fluoride	1–10	0.2 \pm 0.2
Formate	2–23	0.5 \pm 0.5
Phosphate	5–49	0.9 \pm 0.1

Table 1
Linearity ranges and detection limits of the anions analyzed.

ASTM Standard: Recommended operating conditions for the Agilent Capillary Electrophoresis System

Abstract

ASTM Subcommittee D19.05 on Inorganic Constituents in Water approved a new standard test method for determination of dissolved inorganic anions in aqueous matrices using capillary ion electrophoresis and chromate electrolyte¹. The Agilent Capillary Electrophoresis system provided equivalent performance during the inter-laboratory study preceding approval (c/w sect. 17.6 in test method). This document (reference B1.16 in test method) describes equivalent method parameters specific for the Agilent system equipped with DAD detection and computer control through Agilent ChemStation.

Experimental and results

Method parameters

The parameters described here are supplementary to the test method (see also reference 2).

Capillary

Standard bare fused silica capillary (L = 64.5 cm, l = 56 cm, 75 µm id), fitted with a blue alignment interface. A new capillary is prepared by flushing 0.5 N NaOH for 5 min, water for 1 min and run buffer for 3 min (at 1 bar). If the current on a new capillary must be tested (c/w sect. 11.4), a voltage of 18.5 kV should be applied. If the system is idle overnight, leave the capillary in buffer. For long-term storage flush the capillary with water followed by air.

Vials

2-mL glass vials with polyurethane caps are used as buffer or waste container. 1-mL capped polypropylene vials are used as sample container. The buffer vials (inlet, outlet and flush buffer vial) are filled to 1 mL, the waste vial is filled with 0.6 mL buffer. For best migration time stability the run buffer vials should be replaced after 10 runs. It is not recommended to use the replenishment system with the Waters IonSelect™ High Mobility Anion Electrolyte.

Sample preparation

The waste water samples were diluted (1:20) and filtered through a 0.45 µm filter prior to injection.

Agilent 7100 CE verified



Data measured with an Agilent 1600 CE system. Application verified with the Agilent 7100 Capillary Electrophoresis system, showing comparable or even better results.

Results

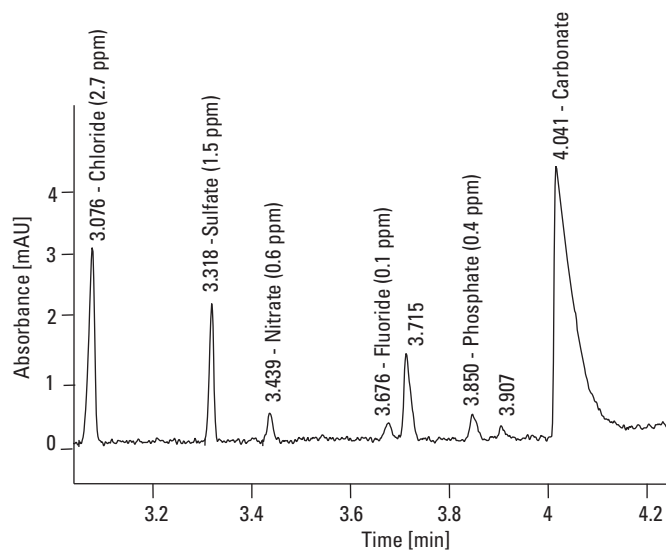


Figure 1
Analysis of waste water from a municipal waste treatment plant.

Method entries

Lift offset: 4 mm
Cassette temp.: 25° C
Preconditioning: Flush 1.1 min from flush buffer vial into waste vial
Electric: On
Polarity: Negative
Voltage: System limit
Current: 0.00 μ A
Power: System limit
Low current limit 0.00 μ A
Time table: 0.3 min, current = 14.00 μ A
Injection: By pressure, 50 mbar x 6.2 sec (37 nL)
UV-detection: Signal = 470/50 nm, reference = 275/10 nm, response time = 0.2 sec (PW > 0.01 min)
Integration: Peak top type = center of gravity
Calibration: Calculate with corrected areas

Monitoring of electroless plating baths by Capillary Electrophoresis

Abstract

Electroless plating is mainly used for the plating of non-metals, for example, ceramics and plastics, and allows the plating of complex shaped parts with a uniform film-thickness. In addition to metal cations, the bath solutions contain additives such as reducing agents (which drive the plating reaction) and organic acids (as buffering and/or metal complexing agents). Inorganic anions are also present as counter-ions of the plating metals. These ions can easily be monitored using capillary electrophoresis (CE) with indirect UV detection.

Experimental and results

Anion analysis was performed using the Agilent Capillary Electrophoresis system equipped with diode array detection and Agilent ChemStation software. Prior to first use, a new capillary was flushed with run buffer for 15 minutes (at 1 bar). Between analyses the capillary was flushed for 4 minutes from an extra buffer vial into waste. Buffer vials were replaced after 10 runs when using 2 mL-vials and after 5 runs when using 1 mL-vials. Sample preparation consisted simply of dilution with water.

Figure 1 shows the analysis of two different plating baths. Electroless nickel-plating baths contain nickel sulfate or nickel chloride, together with hypophosphite as the reducing agent. Formate, present in the electroless copper-plating bath, is an oxidation product of formaldehyde, which is used as a reducing agent. The assay was linear over the range 10–100 ppm with $r^2 > 0.999$. The method detection limit was 1–2 ppm. For the analysis of the electroless nickel-plating bath repeatability ($n = 8$) was $< 0.1\%$ RSD for migration times and $< 4.5\%$ RSD for peak area. The assay also allows the analysis of iron (II) and iron (III) in electro-plating with direct UV detection at 230 nm (data not shown). In the plating bath industry, the monitoring of additives in bath solutions or waste is essential for quality control, cost saving and environmental concerns. Electroless plating bath samples have presented a number of challenges to ion chromatography. CE, in contrast, allows a quick determination of all major components with only minor sample preparation.

Agilent 7100 CE verified



Data measured with an Agilent 1600 CE system. Application verified with the Agilent 7100 Capillary Electrophoresis system, showing comparable or even better results.

Results

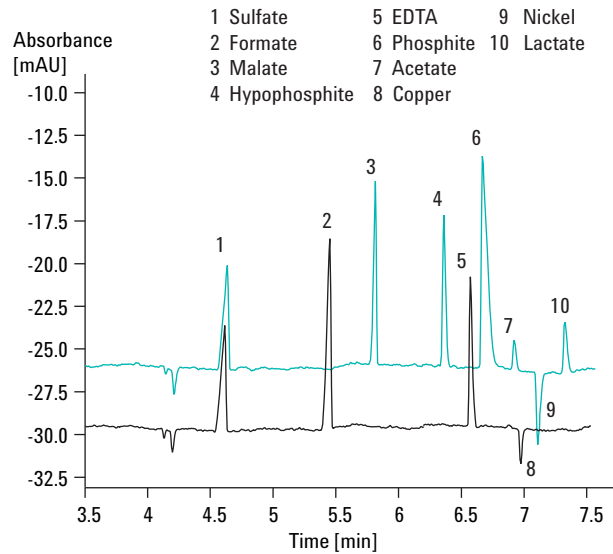


Figure 1
Analysis of electroless nickel- or copper-plating baths.

Electrophoretic conditions

Sample: Electroless nickel-and copper-plating bath, 1:500 diluted with water
Injection: 8 seconds at 50 mbar
Capillary: Fused silica capillary, total length 80.5 cm, effective length 72 cm, internal diameter 50 μm (Agilent part number G1600-62211)
Buffer: Agilent Plating Bath Analysis Buffer (Agilent part number 5064-8236)
Voltage: -25 kV
Temperature: 20 $^{\circ}\text{C}$
Detection: Signal 350/20 nm, reference 275/10 nm

Further reading

Primer

“High Performance Capillary Electrophoresis”

A 180-page lecture-type book explaining the scientific principles and theoretical background of CE – ideal for novice users. Also includes information on separation modes, practical operation and method development.

Agilent publication number 5990-3777EN



Multimedia CD-ROM

“Agilent 7100 Capillary Electrophoresis System”

This CD gives a comprehensive overview of the Agilent 7100 CE system. It includes a searchable application library, product information and a basic introduction to capillary electrophoresis. It also contains useful tools for basic method development and buffer calculation.

Agilent publication number 5990-3980EN

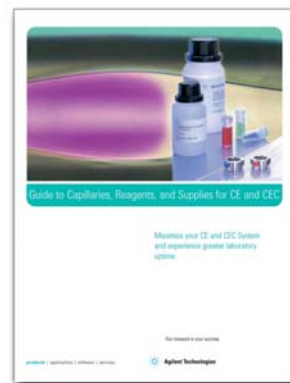


Catalog

“Guide to Capillaries, Reagents and Supplies for CE and CEC”

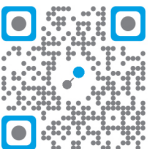
This catalog gives an overview of capillaries, reagents and supplies used for CE and CEC with the Agilent 7100 CE and G1600 CE instruments. It also includes a section on guidance to method development and troubleshooting, and examples of specific applications.

Agilent publication number 5990-3822EN




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Published February 1, 2010
Publication Number 5990-5244EN