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# Determination of soluble anions and cations from waters of pulp and paper mills with on-line coupled capillary electrophoresis

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## Abstract

When the degree of closure of the paper machine wet end waters increases, wet end problems also become more difficult to control without specific and selective on-line measurements. The need to measure the concentrations of individual compounds in order to explain wet end phenomena is growing. This study was performed to set up a CE system to a paper machine and to determine soluble inorganic and organic ions in different locations of pulp and paper process waters with real time analyses by two on-line CE methods. A reconstructed commercial CE apparatus was connected to a papermaking machine via an apparatus, which was a combined sampling and sample pretreatment instrument, the role of which was to filter and dilute the samples before on-line determination by CE. The on-line procedures were optimized for simultaneous determination of anions as chloride, sulfate, oxalate, formate and acetate and for determination of cations as potassium, calcium, sodium, magnesium and traces of aluminium. The quantification was performed with external standard methods using the programs available in the commercial CE instrument. The concentrations of the ions were transferred by using a computerized transfer algorithm exporting the results from the analysis instrument to the process control unit. The developed on-line procedures were tested three times in paper and paperboard mills for 1 month at a time. Correlations were observed between the CE results and changes in the processes. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Paper; Process control; Water analysis; Capillary electrophoresis; Inorganic anions; Inorganic cations

## 1. Introduction

A significant amount of wood material is dissolved and dispersed in mechanical pulping and subsequent bleaching. Since mechanical pulps are seldom well

washed, most of the dissolved and colloidal substances are carried over to the wet end of the paper machine [1].

During paper production, several parameters of the various liquors need to be monitored at different stages of the pulping and paper making processes [2]. For example, the concentrations of oxalate, sulfate and carbonate as well as those of metals in the waters of paper and pulp processes must meet defined criteria to maintain the quality of the process.

Standard methods for measuring summative

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parameters have traditionally been predominant in the analysis of papermaking process waters and effluents. The parameters provide little information on the true chemical character of components. To understand the complex phenomena and mechanisms in the processes, information about individual dissolved components is necessary at the molecular level. Therefore more sophisticated separation and identification techniques are needed [1].

In recent years, the high separation efficiency of capillary electrophoresis (CE) has shown this technique to be an efficient means for reproducible determinations of small anions in pulping liquors [3–5]. In all cases reported sampling, pretreatment and introduction into the capillary have all been performed using off-line technology. Manual handling of the samples may constitute an uncontrollable source of error, especially for oxidation-sensitive ions [2].

Small ions are not easily detected in their native state by UV detectors, which is why CE methods must be developed to enhance their detection and identification. In such analyses the anions are mostly detected with indirect-UV detection when commercial CE instruments are applied.

The aim of this work was to develop a process control system for on-line monitoring of salt levels in the process waters of the pulp and paper industry. Research was performed for measuring dissolvable inorganic anions and cations as well as some organic acids on-line from circulation waters of paper or paperboard machines with CE. For these purposes a commercial CE apparatus was provided with an on-line system for feeding the process samples [6–10].

## 2. Experimental

### 2.1. Reagents

KNO<sub>3</sub>, KCl, CaCl<sub>2</sub> (96%), pyridine and CH<sub>3</sub>COOH were obtained from Merck (Darmstadt, Germany) and glycolic acid, HPCE electrolyte (pH 7.7), NaNO<sub>3</sub> and 18-crown-6-ether were from Fluka (Buchs, Switzerland). NaCl (99.8%) was from Rideld-de Haen (France) and Na<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>·6H<sub>2</sub>O, CH<sub>2</sub>O<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> from J.T. Baker (USA). All

reagents were of analytical grade. The deionized water used for the dilution was purified with a Milli-Q Plus system (Millipore, Bedford, MA, USA).

### 2.2. Instrumentation

A Beckman P/ACE 5000 (Beckman Instruments, Fullerton, CA, USA) CE instrument with UV detection at 254 nm and the facilities to perform on-line process monitoring was used. The fused-silica capillaries were 57–77 cm (effective lengths 50–70 cm) × 50 μm I.D. × 365 μm O.D. from Composite Metal Services (The Chase, UK). The applied voltage was +20 kV (cations) or –20 kV (anions) depending on the method used. Injection was made by a pressure of 0.5 p.s.i. (1 p.s.i. = 6894.76 Pa) for 2 to 5 s. The temperature during the separations was +25°C maintained by a liquid coolant system. The sample carousel of the commercial instrument was provided with a laboratory-made sample flow cell (construction in KCL, Espoo, Finland) and a computerized transfer algorithm with exporting of the results (work done at VTT Chemical Technology, Espoo, Finland) to the control room in the mill.

The conductivities of the electrolyte solutions and that of pulp and paper water produced in method development in the laboratory were measured at +22°C with a Denver pH/conductivity meter Model 20 (Denver Instruments, Denver, CO, USA). Off-line samples were diluted using Milli-Q water (Millipore, Avondale, PA, USA) and filtered through 0.45-μm PTFE membranes (Millipore, Molsheim, France). The combination electrode in pH measurements was calibrated with pH 4.00, 7.00 and 10.00 buffers (Radiometer, Copenhagen, Denmark). The conductivity meter with 1-cm cells was calibrated with an 84 μS/cm KCl solution (Hanna Instruments).

### 2.3. Conditioning of the capillary

The capillaries were conditioned before use with 0.1 M NaOH for 10 min (in on-line measurements for 5 min), with Milli-Q water for 10 min (5 min) and with the background electrolyte solution for 10 min (15 min). Conditioning between runs was made with the electrolyte solution for 5 min (2–3 min).

#### 2.4. Background electrolyte solutions

A commercial HPCE buffer or laboratory-made solutions containing 2.25 mM pyromellitic acid, 6.50 mM NaOH, 0.75 mM hexamethonium hydroxide and 1.60 mM triethanol amine (pH  $7.7 \pm 0.2$ , Fluka) were used. Cations were separated in a mixture of 9 mM pyridine, 12 mM glycolic acid and 5 mM 18-crown-6 ether at pH 3.6.

#### 2.5. Standard mixtures

Reference chemicals were diluted in Milli-Q water to obtain 1000 mg/l stock solutions. The standard mixtures for capillary electrophoretic studies were

prepared from the stock solutions to the concentrations needed to make correlation for quantification and to test the methods.

#### 2.6. Pulp and paperboard waters

The process waters were from three different locations (headbox water, tail water and groundwater) of the paper machine and from one location of the paperboard making machine. They were in-line filtrated through paper filters to get rid of the precipitation and the opalique, and when needed diluted 1:10 or 1:15 with the WIC 100 system (Raisio, Finland, see Fig. 1). Glass fiber Acrodisc syringe filters (Gelman Sciences) with of 1.0  $\mu\text{m}$

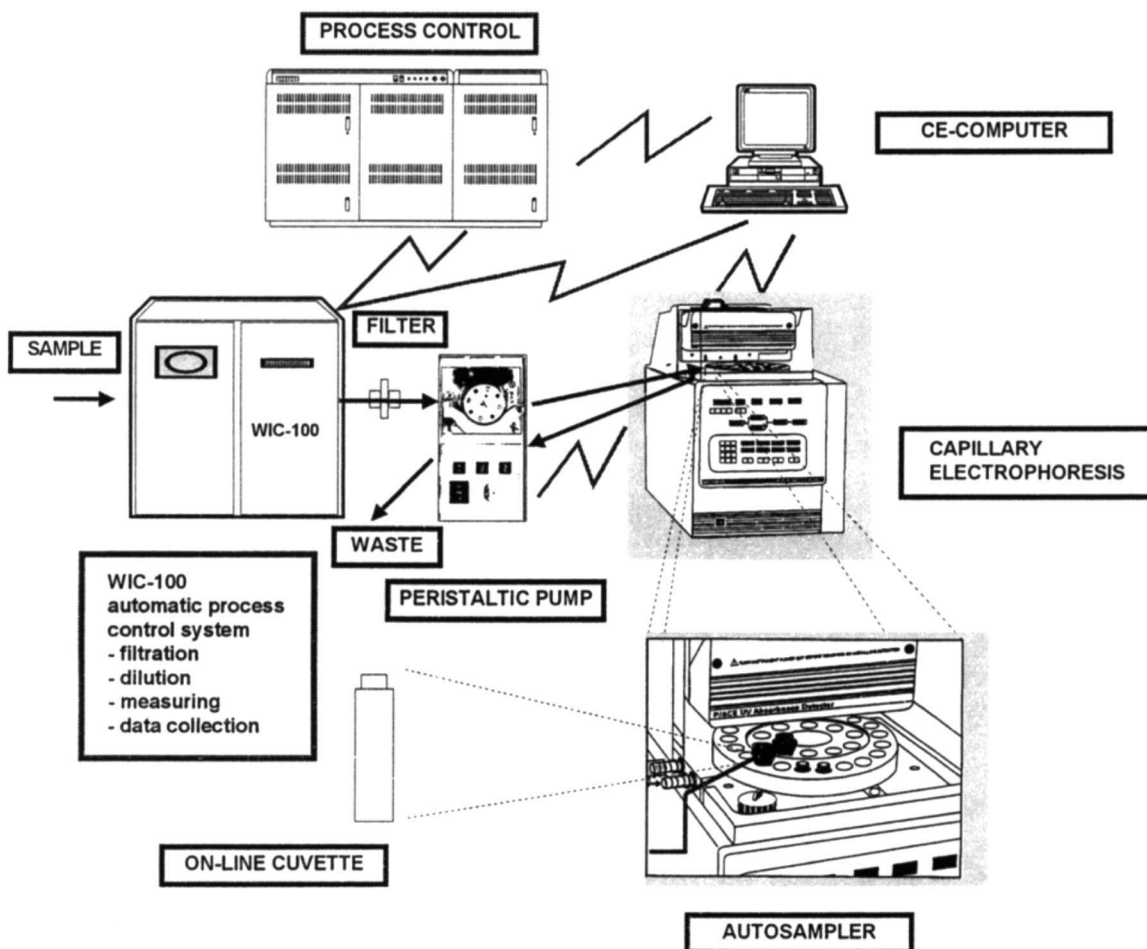


Fig. 1. Scheme of the on-line instrumentation at the mill.

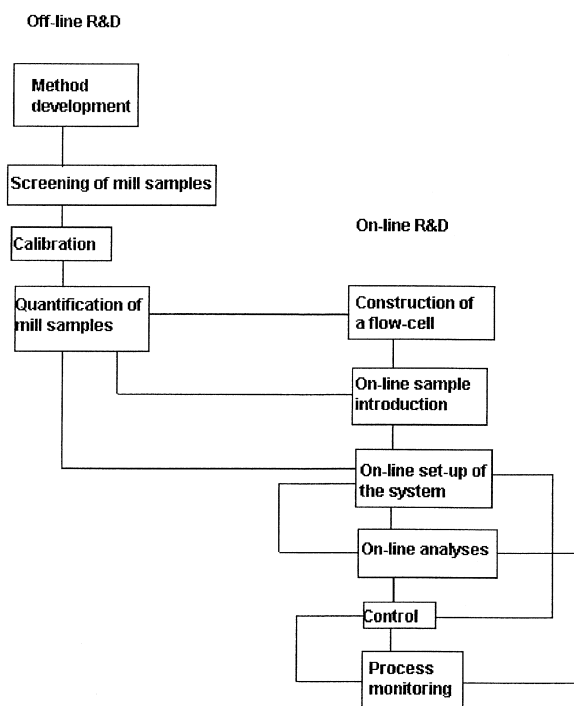


Fig. 2. Scheme of the procedures needed for on-line measurements.

pore size were used to filter the on-line process waters between the automatic measuring system and the CE system. The scheme of the procedures needed for the on-line measurements is compiled in Fig. 2.

### 3. Results and discussion

Separation of the anions was good. Final optimization of the anion separation was made using both the commercial HPCE electrolyte buffer and the laboratory-made buffer in order to obtain the most robust method for the use in the pulp and paper industry. The anion separation system was optimized by the instrumental parameters (length of the capillary, voltage and injection time, Fig. 2). The separation, which was performed within 17 min, showed good reproducibility (1–3%) at the laboratory scale. The migration order of the analytes studied was: chloride, sulfate, oxalate, formate and acetate (Figs. 3 and 4). The robustness of the method was further

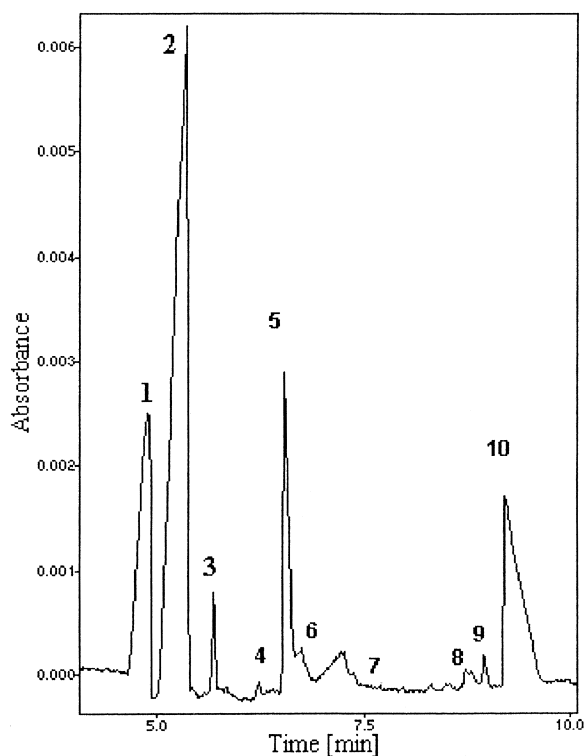


Fig. 3. Separation of anions in the process water of a paperboard mill at pH 7.7 by on-line capillary electrophoresis. Peaks: (1) chloride, (2) sulfate, (3) oxalate, (4–9) unidentified peaks, and (10) formate. Separation conditions described in Experimental.

optimized with  $\text{Br}^-$ ,  $\text{HPO}_4^-$ ,  $\text{F}^-$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_3^{2-}$  reagent additions.

Cations were separated in the laboratory experiments in a sequential mode after anions with an electrolyte buffer (pH 3.6) containing pyridine and 18-crown-6-ether (needed in case of  $\text{NH}_4^+$ ), but could not be performed on-line after anion analysis in the mill. The reason was the manual changeable polarity in the Beckman 5000 instrument, because anion and cation methods use opposite polarities. Therefore, anions and cations were analyzed independently in the three-mill trial. Fig. 5 shows that potassium migrated first followed by calcium, sodium and magnesium. The analysis could be best performed within 10 min, but was reduced to 5 min in the on-line measurements. To see the separation efficiency, the robustness of the method was further optimized with  $\text{NH}_4^+$ ,  $\text{Li}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  chemical additions.

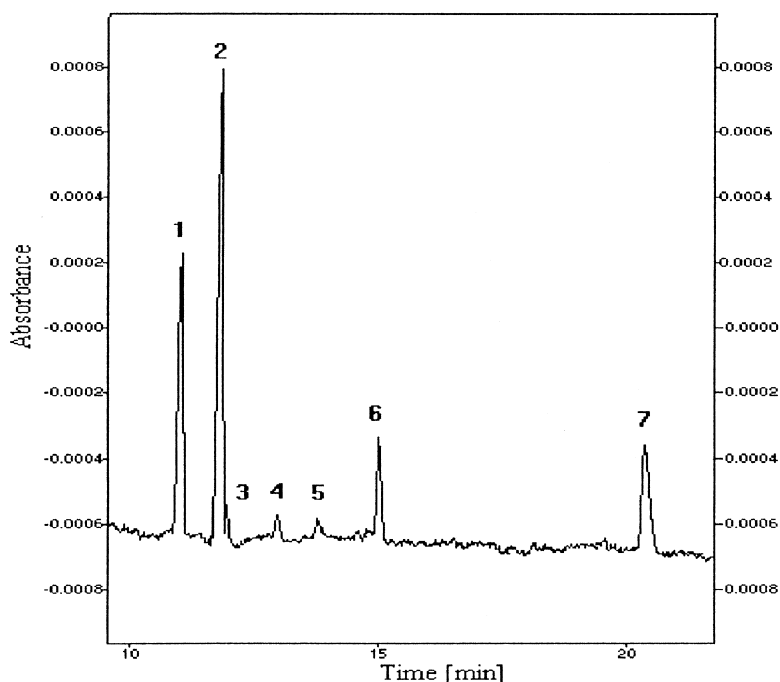


Fig. 4. Separation of anions in the process water of a paperboard mill at pH 7.7 by off-line capillary electrophoresis. Peaks: (1) chloride, (2) sulfate, (3) unidentified peak, (4) oxalate, (5) unidentified peak, (6) formate and (7) acetate. Separation conditions described in Experimental.

When the system was set up for on-line measurements, the separation efficiency of anion analysis could be decreased even more by time, but the operation made sulfate and nitrite comigrate. However, their sum concentration gave only a minor error on the concentration of sulfate, since the origin of nitrite was from the wood material itself and its concentration was low giving only a 0.5–3% error in monitoring process.

### 3.1. Quantification

The linearity validation was performed at the laboratory scale with standards and process waters obtained from the mills (Fig. 2). The analyses were carried out for each of the ions with six repetitions and nine concentration levels. The response factors (RF values) were used for quantification of the anions and cations in the mills trials. The RF values were calculated from the concentration calibration curves by using the mean concentration value of the average amount of the ion in the papermaking

waters. The average values were estimated by running mill waters from four different factories at the laboratory-scale.

The reproducibility of the separations was moderately good: relative standard deviations for the absolute migration times of anion standards analyzed in the laboratory were below 6% and those of the cations varied from 1 to 4% depending on the concentration of the ion. When high concentrations were measured, the reproducibility was poorer. This was also noticed in on-line analyses using undiluted process water samples. The limits of detection (LODs) calculated using standards were low, being in the order of 0.5 mg/l or slightly lower using a 5-s injection time at 0.5 p.s.i. The detection limits were measured by calculating the analyte concentration at a signal-to-noise ratio ( $S/N$ ) of 3. The concentrations of the ions in papermaking waters are rather high and therefore special instrumental optimization was not needed to obtain a system sensitive enough for the measurements.

Sulfate (Figs. 3 and 4, Tables 1 and 2) and sodium

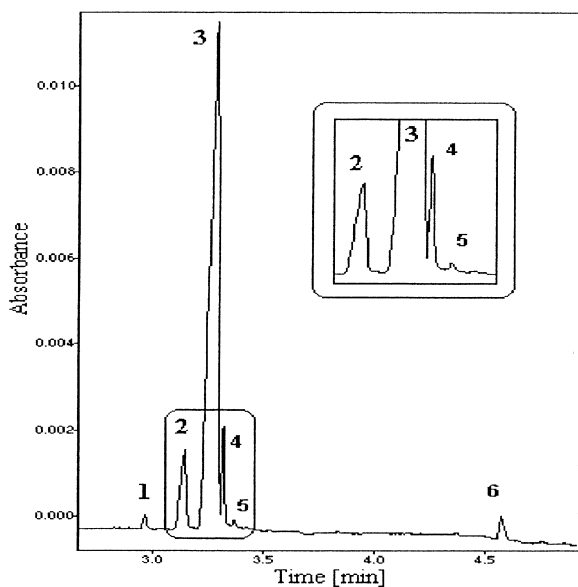


Fig. 5. Separation of cations in the groundwater of a paper mill at pH 3.6. Peaks: (1) potassium, (2) calcium, (3) sodium, (4) magnesium and (5) possibly aluminium. Separation conditions described in Experimental.

(Fig. 5, Table 1) were the main ionic components in process waters of paper and paperboard mills. Sulfate originates mainly from sulfuric acid used to control the pH and from aluminium sulfate used in the flocculation of harmful compounds. Aluminium

Table 1  
Concentrations of ions in a papermaking process<sup>a</sup>

Papermaking waters	Ion detected	Concentration (mg/l)
Headbox water	Chloride	22
	Sulfate	540
	Nitrite	17
	Potassium	3
	Calcium	43
	Sodium	190
	Magnesium	12
Tail water	Chloride	28
	Sulfate	640
	Nitrite	3
	Potassium	3
	Calcium	57
	Sodium	230
	magnesium	9

<sup>a</sup> Determinations made with an off-line technique.

Table 2  
Concentrations of ions in a papermaking process<sup>a</sup>

Sample	pH	$\kappa$ (mS/cm)	SO <sub>4</sub> <sup>2-</sup> (mg/l)
Tail water	6.5	1.6	440
Tail water	7.1	1.6	420
Tail water	4.4	1.2	680
Headbox water	7.5	1.5	350
Headbox water	7.5	1.4	430
Headbox water	4.4	1.2	680
Headbox water	5.4	1.0	520
Ground water	4.3	1.1	750
Ground water	6.0	0.8	590

<sup>a</sup> Determinations made with an off-line technique.

can also be seen in the electropherogram of process water from a paper mill (Fig. 5).

For reference, the concentrations of all the ions obtained with CE were cross-checked with inter-laboratory tests made by ion chromatography (IC) using two off-line samples obtained from a mill. The average differences of the results obtained with CE and IC were 1–13% (Table 3).

### 3.2. On-line determinations in the mills

On-line determinations of anions and cations in pulp and paper mills were tested in three periods during 1 year. The test showed that it is possible to adapt a laboratory CE system for on-line measurement of pulp or paper machine wet end waters. In

Table 3  
Correlation of the results obtained in determinations of sulfate made on-line (CE) at a paper mill and off-line in the laboratory (IC)

Sample	On-line CE sulfate (mg/l)	Off-line IC sulfate (mg/l)	Difference (%)
Groundwater (seq. no 335)	1043	1007	4
Groundwater (seq. no 337)	1027	1008	2
Groundwater (seq. no 339)	1007	1095	9
Groundwater (seq. no 340)	701	709	1
Tailwater (seq. no 341)	747	651	13

these three mill trials over 2000 on-line samples were analyzed, with over 9000 anion and cation determinations.

Two mill trials have been carried out on a paper machine producing coated, wood-containing papers and one on a paperboard machine. In both mills a WIC 100 system was available for the sample pretreatment and data collection. In the first trial, only sulfate was determined (Table 1). Over 300 samples were analyzed from the three process water lines and the results were fed automatically into the mill's data system. In the second trial, sulfate, oxalate and formate were determined about 800 times from on-line samples from the same lines. The third trial was carried out at a paperboard mill so that one of the three lines came from the pulp mill. Over 1100 samples and 7000 determinations were performed. Both anions and cations were measured, but the periods of cation measurement were only 2 days.

It was noticed that when anions were determined, the process water samples from the paper machine had to be diluted to prevent the overloading effect of the sulfate zones. However, samples could be analyzed without dilution in the case of paperboard mill trials.

The results showed a correlation between the changes in paper making processes and the concentration variations of the measured ions. Figs. 6 and 7 show the concentrations of sulfate and oxalate over a period of 1 month during the CE measurements in the paperboard mill. In the case of sulfate (Fig. 6), three increasing concentration levels can be seen around the samples with the numbers 50, 170 and 250. A similar pattern can be seen in the case of oxalate (Fig. 7). This increase results from the manufacturing of paper products with higher square weight, which usually also means higher consumption of process chemicals such as sulfate. Occasional changes may be the results of disturbances in the processes. The concentration level of oxalate is low because of its poor solubility in water.

#### 4. Conclusions

Our studies showed that two carefully optimized CE methods were very suitable for the determination of the anions chloride, sulfate, oxalate, formate and acetate, and also for the cations potassium, calcium, sodium and magnesium. Aluminium could also be

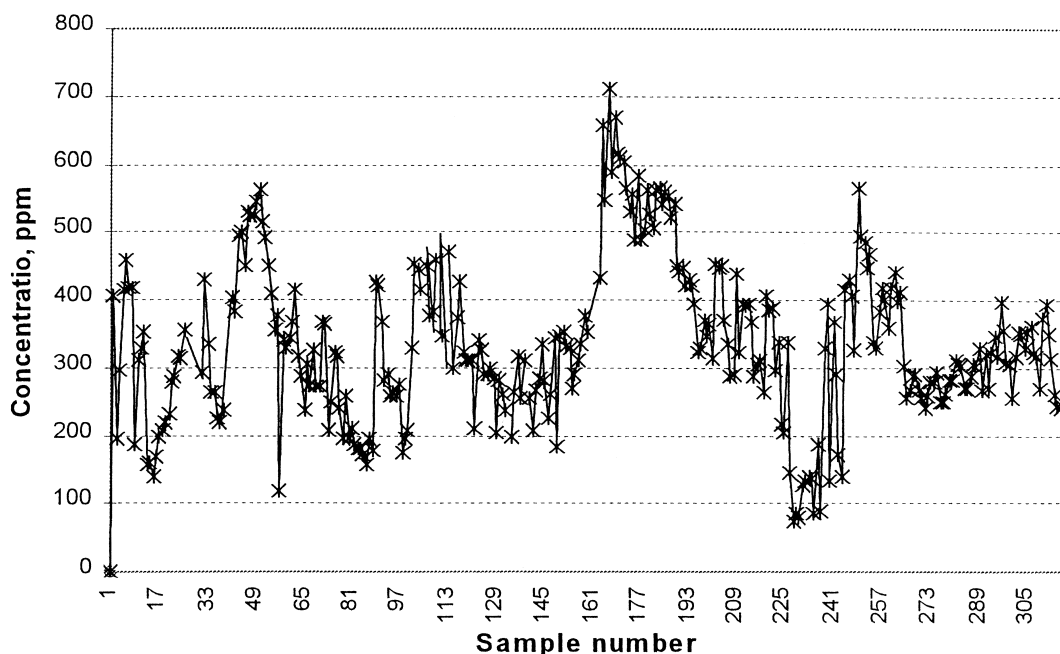


Fig. 6. Concentration of sulfate in the process water of a paperboard machine over a period of 1 month (10 May–17 June 1999).

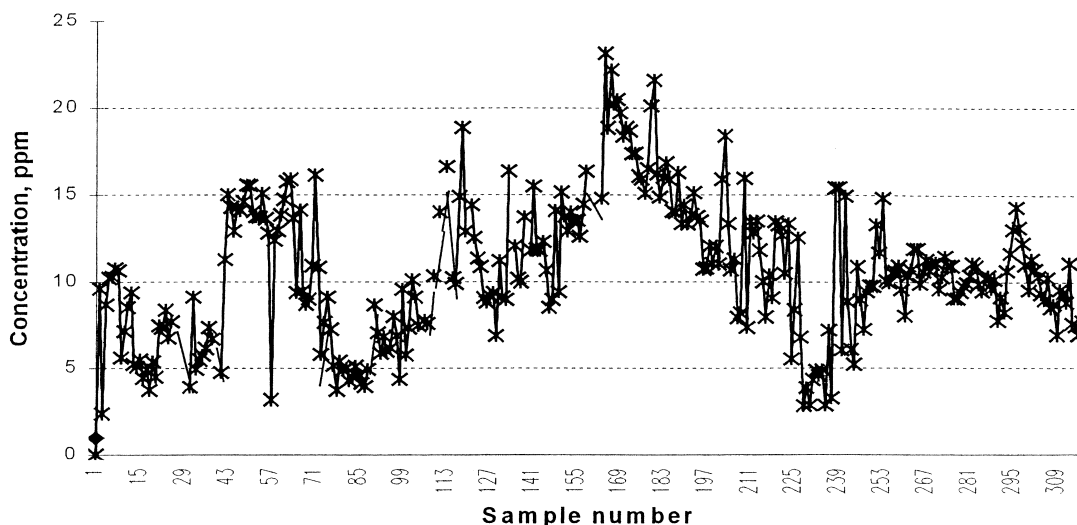


Fig. 7. Concentration of oxalate in the process water of a paperboard machine over a period of 1 month (10 May–17 June 1999).

monitored. The relative standard deviations of the quantitative results calculated with eight replicates (four injections) were below 6%.

The routine, real time on-line screening method of pulp and paper mill waters has been used in paper and paperboard mill to:

1. Simultaneously quantitate chloride, sulfate, oxalate and formate.
2. Simultaneously quantitate potassium, calcium, sodium and magnesium.
3. Reproduce data processing methods to export the results to the process control units of mills.
4. Identify disturbances in processes and changes in ionic concentrations resulting from changes in papermaking processes.
5. High throughput screening with on-line coupled CE.
6. Real time data processing with automatization.

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