

On-line process monitoring of water-soluble ions in pulp and paper machine waters by capillary electrophoresis

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Abstract

In this study, capillary electrophoresis (CE) was used for separation of inorganic and organic ions from waters of paper and paperboard machines at mills. The instrument was constructed for on-line measurements by building a batch-type sample feeding unit. Chloride, thiosulphate, sulphate, oxalate, sulphite, hydrogen sulphide, formate, carbonate, phosphate and acetate in the process water samples were separated using an ion-specific separation system in CE with dicarboxylic acid buffer (pH 8.2), with pyridinium-2,3-dicarboxylic acid modified with commercial NICE-Pak OFM-OH solution (pH 12.0) or with a cetyltrimethylammonium bromide solution modified with chromate (pH 10.6). In addition, Analis CEofix Anions 8 electrolyte solution was tested in on-line studies at mills. It allowed 5 min separation time for the anions. Aluminium was determined at pH 3.6 in 10 min by using a laboratory-made imidazole buffer modified with 18-crown 6-ether. The developed CE systems were used to monitor the concentrations of sulphur species in dithionite degradation, to estimate corrosion degree in the water tanks, to monitor formaldehyde as the biocide chemical in wire washing and, in general, to observe process disturbances resulting from chemical feedings and their sites. The CE combination was on-line coupled to eight different process machines for continuous monitoring of concentrations for periods between two weeks and one month at paper and pulp mills in Finland.

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1. Introduction

The future requirement to close water circulation in paper machines during production will increase the concentrations of water-soluble compounds in the system. Most probably, water circulation will lead to chemical precipitation and steel equipment corrosion in the machines, where the chemicals will be concentrated. Optimal consumption of process chemicals in the production will be more difficult to control without selective, sensitive and sufficiently rapid on-line measurements. It has been estimated that the number of analytical measurements made from the water of one paper machine during one day can be increased to 15,000–20,000, mostly being physical measurements.

Most of the chemical and physical measurements provide valuable information about the processes. There will be a need for separation techniques such as liquid chro-

matography (LC), ion chromatography (IC) or capillary electrophoresis (CE) to verify the concentrations of individual ions. Particularly, on-line chemical measurements are focused on monitoring pH and conductivity [1]. Usually, these basic methods involve the measurement of summative parameters. They are traditionally predominant in the determination of papermaking process waters and effluents, because they are simple and rapid measuring techniques. However, the results obtained with these measurements provide only minor information about the chemical behaviour of individual ions and compounds. Therefore rapid, powerful, high-throughput and specific identification techniques, such as capillary electrophoresis [1–3] with ultraviolet absorption (UV) detection, are needed for on-line separation and simultaneous determination of compounds.

The determination and identification of water-soluble ions and neutral compounds are needed to explain wet end phenomena in paper processes. For example, aluminium sulphate, alum, is used for flocculation of detrimental extractives in board sizing. Other targets of alum usage are

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to act as a mordant of dyes, to act as a retention aid, to minimize pitch problems and to control pH [4].

Chemical reagent additions are made to the wet end process waters in paper production and pulp production [3]. Therefore, these waters may contain not only large concentrations of sulphur species but also of other inorganic ions and organic compounds. These water solutions containing sulphur compounds have been found to be corrosive towards the steel used in the storage tanks. The most corrosive species are ions such as chloride and thiosulphate. These can be measured by capillary electrophoresis. Organic acids may also be corrosive towards steel, although usually not in basic media. Furthermore the process waters of pulp mills contain sulphate and sulphite, which can also be monitored by CE [2–4]. Dithionite is corrosive, but normally decomposes rapidly in process waters, forming sulphite, thiosulphate and sulphate. To minimize costs the water tanks can be made of carbon steel, which is considered to be a non-reactive material at high pH. However, some tanks require replacement after only 3–5 years, whereas others may still be functional after 15 years. The drawback of the closed water circulation in paper machines is that, according to Kapoor et al. [5]. It has been supposed that when chloride and thiosulphate are simultaneously present in certain concentration ratios in processes they can be aggressive towards stainless steel even at neutral pH. This is a real problem, since many paper processes use basic media.

The use of dithionite (hydrogen sulphite) is technically advantageous. Dithionite bleaching reduces chromophores of lignin and is thus a reductive bleaching method for low brightness paper qualities such as SC, newspaper, catalogues, some LWC and de-inking. The pulp yield is high, 99–100%, and bleaching does not need expensive investments. Optimum conditions for dithionite bleaching have been proposed to be: pH 4.5–6.5, temperature 50–70 °C, consistence 3–5%, dosage 0.5–1% and reaction time about 1 h. The disadvantage is that sodium dithionite is unstable at low pH. Decomposition of dithionite can be aerobic or anaerobic. Some breakdown products may be malodorous. Dithionite can also react with pulp material, whereafter its breakdown reactions are different compared to decomposition in liquid phase [4,6]. Thiosulphate, one of the breakdown products of dithionite solution, is very corrosive.

Some sulphur compound (e.g. sulphate) concentrations can be high in paper processes, due to the chemical additions and oxygen that is absorbed in pulp. The stability of dithionite depends on the storage time and its concentration in the process water. The formation of thiosulphate in closed water circulation can reach the so-called critical corrosion concentration level, which in the case of tail water is 10 mg/l [7,8]. Even at concentrations as low as 5–10 mg/l it can result in corrosion problems in paper machines.

In this research concentrations of sulphate and thiosulphate were monitored by short-term sequential CE measurements coupled to an on-line sampling system. Continuous

monitoring of sulphite was difficult because sulphite can react with oxygen accumulated in a buffer electrolyte. A better technique to determine the concentrations of sulphur compounds in paper machine process waters can be helpful in reducing corrosion and in optimizing consumption of dithionite. The optimal consumption of chemical additives that are used in mills can lead to remarkable cost savings in pulp and paper processes.

The other aims of the project were to develop CE methods for on-line monitoring of chloride, thiosulphate, sulphate, oxalate, sulphite, hydrogen sulphide, acetate, carbonate, phosphate, aluminium and formaldehyde in order to monitor the behaviour of individual ions in the processes. Typical anions that form precipitates with calcium as counter-ion in pulp and paper mills are oxalate, sulphate and carbonate. Thus it was important to develop a continuous process separation method to monitor the concentration levels of these anions.

2. Experimental

2.1. Reagents

KNO₃, KCl, CaCl₂ (96%), pyridine, Na₂HPO₄·H₂O, formaldehyde, imidazole, Na₂CO₃ and 0.1 M NaOH (Titrisol) were obtained from Merck (Darmstadt, Germany) and glycolic acid, HPCE electrolyte (pH 7.7), NaNO₃, potassium chromate, Al₂(SO₄)₃ and 18-crown-6-ether were from Fluka (Buchs, Switzerland). NaCl (99.8%), Na₂SO₃ and Na₂S₂O₃ were from Riedel-de Haen (France). Na₂SO₄ was from J.T. Baker (Deventer, The Netherlands). CH₂O₂, C₂H₂O₄, cetyltrimethylammonium bromide (CTAB), pyromellitic acid (PMA), pyrazine-2,3-dicarboxylic acid (PyDC) and NaS·10H₂O were from Sigma-Aldrich (Steinheim, Germany). The commercial NICE-Pak OFM-OH Anion-BT was from Waters (Waters, Milford, MA, USA). CEofix Anions 8 (pH 8.2) was obtained from Analis (Belgium). All reagents were of analytical grade. The deionized water used for dilution was purified with a Milli-Q Plus system (Millipore, Bedford, MA, USA).

2.2. Instrumentation

P/ACE 5000 and MDQ capillary electrophoresis instruments (Beckman-Coulter, Fullerton, CA, USA) with UV detection at 254 and 280 nm were used. Identical instruments were used independently in two laboratories or simultaneously in the laboratory and at a mill. Only one of them at a time was used for on-line determinations at the mills.

The sample carousel for the CE instrument was equipped with a sample flow cell constructed in The Finnish Pulp and Paper Research Institute (KCL, Espoo, Finland) to provide on-line sampling from the processes. The fused silica capillaries [50–80 cm total length (40–70 cm effective

Table 1
Instrumentation and conditions in the laboratory (optimized conditions)

Apparatus (CE)	P/ACE 5000 and P/ACE MDQ
Capillaries	50–67 cm × 50 μm × 365 μm (anions and cations) 37 cm × 50 μm × 365 μm (aluminium)
Detection	UV 254 and 280 nm (both indirect)
Voltage	20 kV (− → + anions), 25 kV (+ → − cations), 17 kV (+ → − sulphur compound)
Temperature	25 °C (cartridge, sample tray), 20 °C (cartridge, sample tray, sulphur compound)
Injection (inlet)	0.5 p.s.i. for 3–5 or 10 s (sulphur compound)
Electrolyte solutions	CEofix Anions 8 (Analix), pH 8.2 CTAB-chromate, pH 10.6 (developed at VTT) OFM–OH–pyrazine-2,3-dicarboxylic acid, pH 12.7 (developed at VTT) Imidazole, pH 3.6 (developed at VTT, cations and aluminium)

length) × 50 μm i.d. × 365 μm o.d.] were from Composite Metal Services (The Chase, Hallow, Worcester, UK). Samples were introduced to the capillary by pressure. Details of the experimental conditions are presented in Tables 1 and 2.

Glass fiber Acrodisc syringe filters (Gelman Sciences, Ann Arbor, MI, USA) with pore size 1.0 μm were used to filter the on-line sample solutions in the line between the sample transfer pump and the CE. In Fig. 1 its place was in the filtrate line after the 3-way vessel, which is before the dilution pumps.

The experimental parameters were optimized beforehand in the laboratory with the CE instrument used at the mill. Further optimization was still needed when the CE was performing on-line sampling and analyses of the process samples.

Table 2
Instrumentation and conditions at the mill trials

Apparatus (CE)	P/ACE 5000 and P/ACE MDQ
Capillaries	20–57 cm × 50 μm × 365 μm (anions and cations)
Temperature	25 °C
Voltage	−20 kV (anions); +20 kV (cations)
Injection	5 s
Detection	Indirect 280 or 254 nm
Electrolyte solutions (anions)	CEofix Anions 8 (Analix), pH 8.2 or PMA 7.7 (laboratory-made, KCL)
Electrolyte solution (cations)	Imidazole, pH 3.6 (developed at VTT)
Analysis time	Total 15–30 min; CE 5–20 min
On-line system	Laboratory-constructed
Sample vial	Laboratory built continuous flow-through type
Pumps	Peristaltic pump (ISCO Inc.)
Filtrations	Ceramic filter 0.2 μm, length 25 cm (USF)
Sample handling and dilution	Peristaltic pumps or gradient programmer (ISCO)

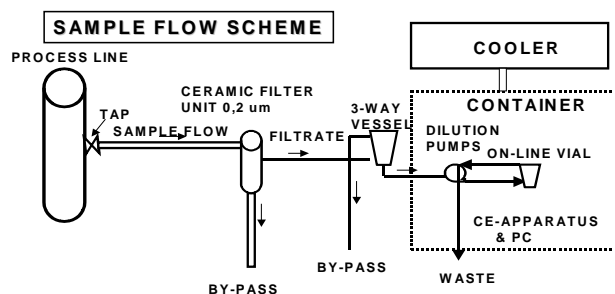


Fig. 1. Scheme of process sample flow in on-line capillary electrophoretic measurements.

2.3. Conditioning of the capillary

In the laboratory tests the capillary was conditioned before use by rinsing it with 0.1 M NaOH, with Milli-Q water and with the background electrolyte solution used in separations as described elsewhere [1,2].

2.4. Background electrolyte solutions

In the optimised CE method the anions were separated with a commercial CEofix Anions 8 solution (pH 8.2), with laboratory-made solution containing 10 mM PyDC 0.5 mM OFM–OH solution (pH adjusted with 0.1 M NaOH to 12.0), with 10 mM CTAB 0.5 mM chromate (pH 10.6) or with laboratory-made PMA solution (pH 7.70 at 24.3 °C) containing 2.25 mM pyromellitic acid, 6.50 mM NaOH, 0.75 mM hexamethonium hydroxide and 1.60 mM triethanol amine [1,2]. The optimised CE separations of aluminium from calcium, sodium, magnesium and manganese were performed in a mixture of 9 mM pyridine–12 mM glycolic acid–5 mM 18-crown-6-ether at pH 3.6 with or without methanol [optimized to 30% (v/v) of the electrolyte volume] [2].

2.5. Standard mixtures

Pure reference materials were diluted in Milli-Q water (ambient temperature) to obtain 1000 mg/l stock solutions. The working mixtures for capillary electrophoretic studies were prepared from the stock solutions to the concentrations needed in quantification and method testing. However, the stock solutions of sulphur compounds, chloride, oxalic acid and acetic acid at concentrations of 10,000 mg/l were prepared in freshly boiled and cooled Milli-Q water to minimize oxidation of the sulphur compounds. The standards and the off-line samples were all filtered before use through 0.45 μm PTFE membranes (Millipore, Molsheim, France).

2.6. Samples

Process waters samples were obtained for laboratory measurements from the mills. The waters were diluted, when the concentrations of sulphate or sodium were above 200 mg/l. The separation parameters were optimized beforehand in the

laboratory with the CE instrument used at the mill. Pulp water samples were filtered with syringe filters (PTFE, 0.45 μm pore size, 25 mm diameter, Acrodisc, Pall Gelman, Ann Arbor, MI, USA) before analyses.

At mill the samples were siphoned from the process water tanks. They were filtered with a ceramic filter tube, pumped with a peristaltic pump through Teflon tubing to the CE instrument. They were filtered on-line and diluted (1:2, 1:5 or 1:10 if needed) with water before purged into an on-line suitable sample vial (Fig. 1, the flow-vial was laboratory-made by KCL). All the steps were done on-line and they were sequentially performed with the CE instrument connected to a process water tank at mill.

3. Results and discussion

3.1. Laboratory-scale measurements and optimization

The aims of the laboratory studies were to optimise capillary electrophoretic methods for the determination of sulphur-containing anions and other inorganic anions as well as organic acids and aluminium in paper and cardboard machine waters and to get the methods ready for use in on-line measurements at the mills. The laboratory optimization was made with reference mixtures simulating the real process samples. The parameters optimized during the test were electrolyte compositions, sample dilution and experimental parameters. In addition, the effect of aerobic conditions in measurements of sulphur compounds was observed.

Three methods were evaluated by laboratory optimization in order to find the most useful method for the on-line measurements, e.g. short analysis time, low detector noise, reproducible separation. The background electrolyte solution (BGE) containing 10 mM PyDC and 0.5 mM OFH-OH⁻ (pH 12.0) was the most stable. However, when $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} and SO_3^{2-} (Fig. 2A) were separated with the BGE, a high step in the detector signal could be noticed. However, quantification was possible, since separation and the detector profile were reproducible. To compare the CE results obtained with standardized method, commercial CE electrolyte solution (Anions 8, pH 8.2) was used. Anions in the process samples were separated with a buffer having pH 8.2 (Fig. 2C), since it allowed the fastest separation for the analytes. Electrolyte solution made of CTAB and chromate (at pH 10.6) allowed good sensitivity for the analytes. In addition, the separation of sulphur compounds was reproducible (Fig. 2C). However, S^{2-} and SO_3^{2-} co-migrated in this BGE, which is why their limits of quantification could not be determined. Reliability of the methods was tested with process samples monitoring the migration times of the analytes. Good results were obtained, since the values increased within 25 runs only with 1.34–1.98%. The results showed that sulphite was oxidized under chromate solution in off-line studies. Because of that antioxidants were used in the samples and the buffers.

Two CE electrolytes were also tested for the on-line determination of aluminium in process waters of a cardboard machine at mill. The buffers used for the separation of aluminium from calcium, sodium, manganese and magnesium were 9 mM pyridine 12 mM glycolic acid 5 mM 18-crown-6-ether (pH 3.6) and the same electrolyte solution with methanol (methanol–water, 30:70, v/v). Aluminium was identified with indirect UV detection. Sufficient sensitivity for aluminium in the electrolyte system was obtained with an injection of 2 mg/l for 3 s at 0.5 p.s.i. (1 p.s.i. = 6894.76 Pa) pressure. Linear correlation between its peak area and concentration was obtained over a concentration range of 5–30 mg/l (Fig. 3). By using the calibration line concentration of aluminium in five water samples (one white water, one random water and three waters from different depths in the tanks) obtained from KCL were measured and the values were from 10 to 23 mg/l. The process samples that were also spiked with 12.3 mg/l aluminium sulphate gave the recoveries for aluminium between 42 and 69% in BGE without methanol and 66–127% in BGE with 30% methanol.

3.2. On-line mill studies

The dosage of aluminium to process waters was made by using 5–15% aqueous solution of aluminium sulphate. Changes in its concentrations was on-line monitored from process samples at a cardboard machine by using the CE electrolyte containing 30% methanol in it. CE results obtained showed that when the site of aluminium sulphate dosage changed in the process it greatly affected the aluminium concentrations recognized in the CE measurements (Fig. 4). This was tested in a two days period at the cardboard machine, when aluminium was added to the process tube at random dosage sites. Fig. 4 shows that the measured concentrations of aluminium fluctuated during these two days. We assumed that the most probable reason for the wide fluctuations was inadequate mixing of aluminium in the process water before sampling. It was also assumed that adherence of aluminium to the inner surface of the process pipeline can show fluctuations of aluminium concentration. We could measure CE results during a longer period, too. They showed that it took some days for aluminium concentration to become stabilized after a large reagent addition.

3.3. Dithionite bleaching

Concentrations of sulphate, thiosulphate and sulphite were monitored in dithionite bleaching at a paper mill. The most of the sulphur compounds are formed in decomposition of dithionite, when it is oxidized during dithionite bleaching, e.g. paper production (Fig. 5). It is important to determine thiosulphate concentration, because sulphur has been found to promote corrosion of steel vessels at high temperatures. For these studies both the laboratory-made PMA solution and the commercial CEofix Anions 8 solution were used.

3.4. Disturbances

Dithionite could not be analysed in off-line, because it was oxidized to thiosulphate, sulphate and sulphite in OFM-OH⁻ pyrazine-dicarboxylic acid solution. However,

from fresh samples dithionite and sulphide could be monitored in CTAB-chromate electrolyte.

A break in dithionite feeding in process causes an increase in the concentrations of its decomposition products due to its fast oxidation in aerobic bleaching conditions. Fig. 6 gives

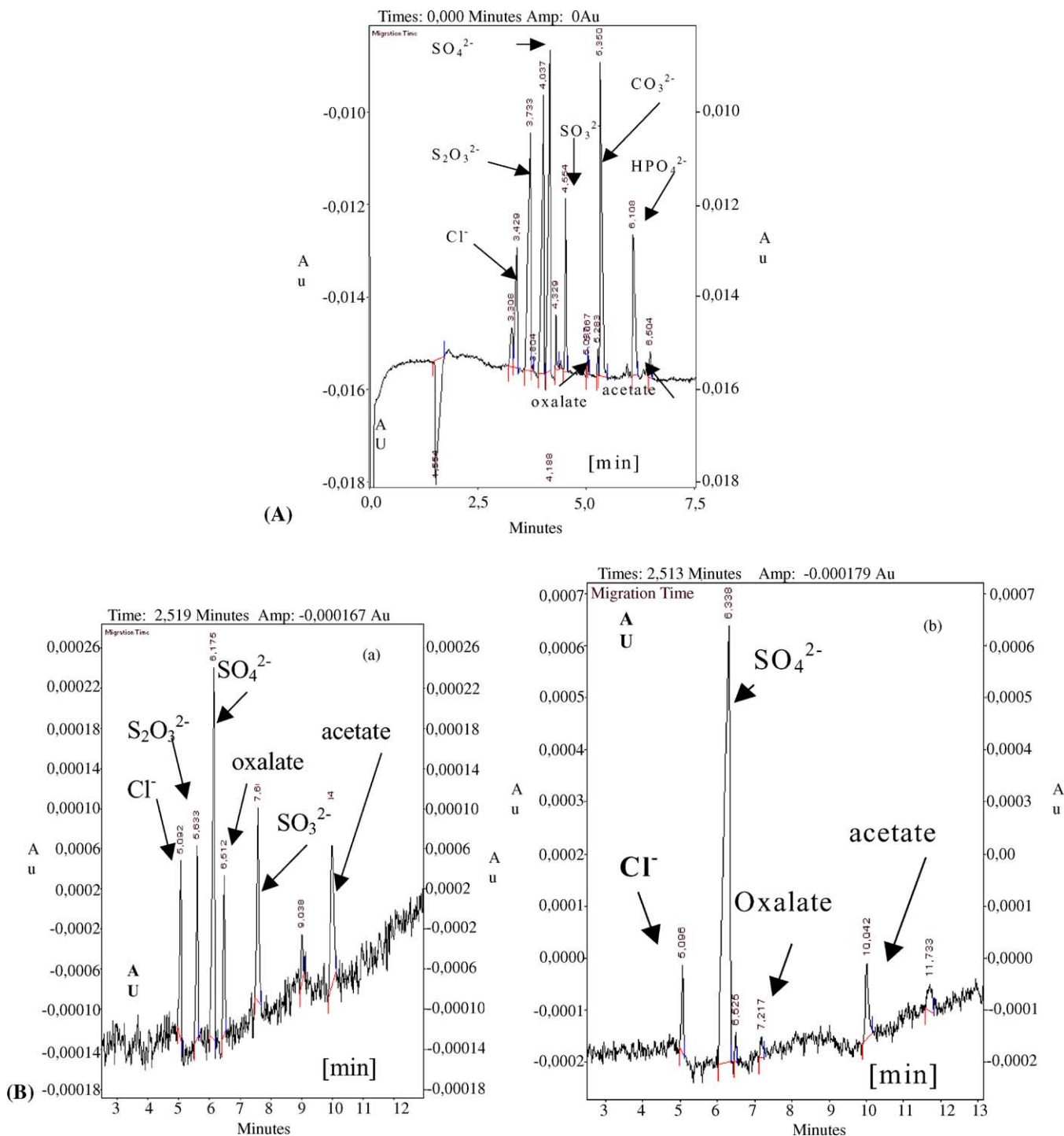


Fig. 2. (A) The electropherogram of the standard mixture. BGE: 10 mM PyDC, 0.5 mM OFH-OH⁻, pH 12.0, separation conditions as listed in Table 1. The other peaks were unidentified. (B) The electropherogram of the standard mixture. BGE: Anions 8, pH 8.2, separation conditions as described in Table 1; peak numbering as in (A); (b) the electropherogram of the process water sample from a paper mill. (C) Off-line separation of process waters: (a) groundwater; (b) water from the mixing chamber and (c) white water; electrolyte solution CTAB (see experimental).

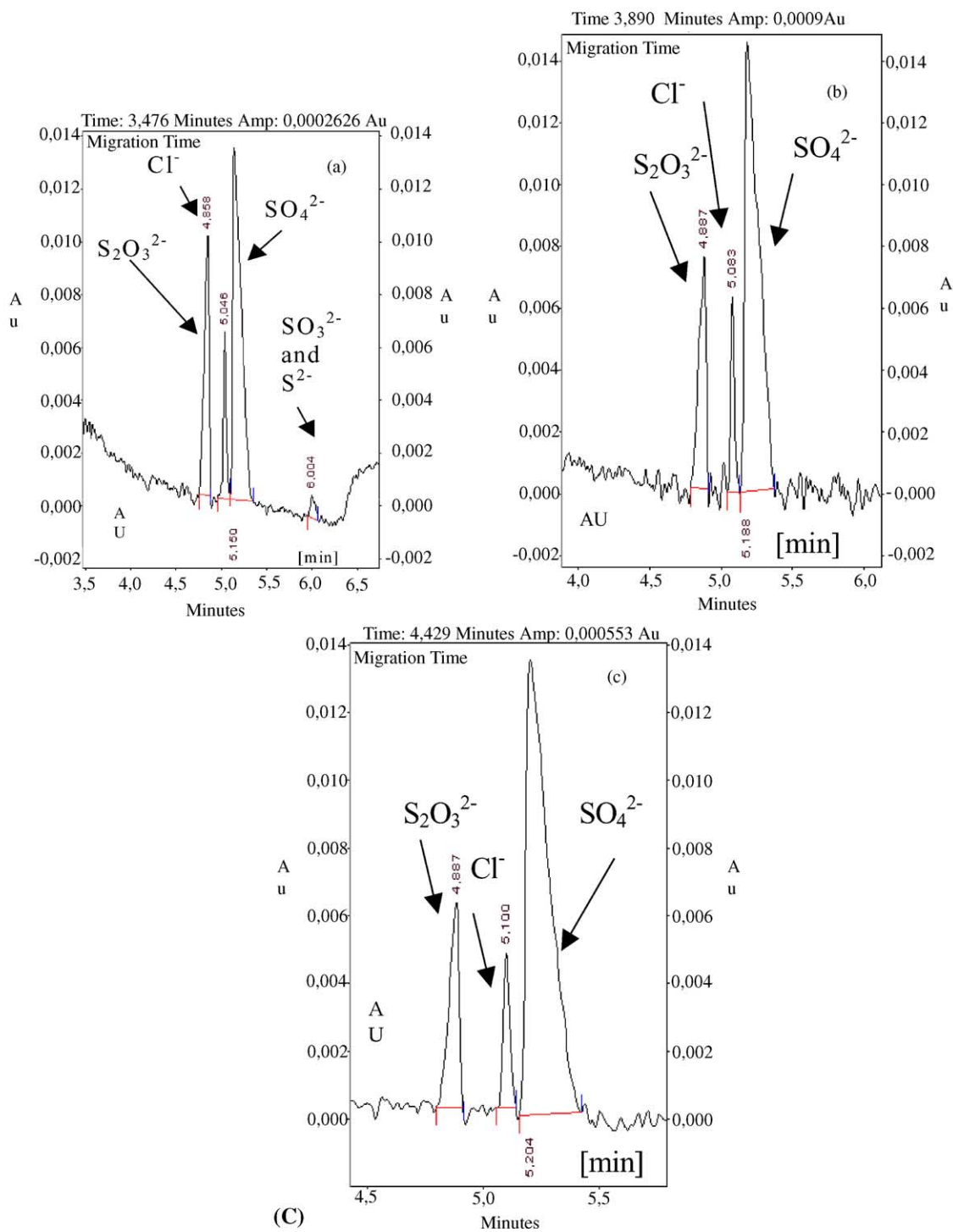


Fig. 2. (Continued).

the concentrations calculated within five days period when the CE equipment was on-line monitoring the concentrations of sulphur compounds. It was noticed especially at the concentration of thiosulphate that its amount in the system increased at the beginning of the measurement period, but at the end the concentration level was again stabilized to normal. The reason for the contemporary increase was noticed to be a disturbance in dithionite dosage. During this

low feeding period dithionite was oxidized to thiosulphate. We observed that thiosulphate concentration in a paper machine, which was on-line coupled through the sampling units with our CE equipment, was generally above the so-called critical concentration level for corrosion, i.e. 10 mg/l in the case of the corrosion indicator thiosulphate [6].

Usually, the actual feeding breaks of dithionite chemical in paper machine operation were not noticed in the

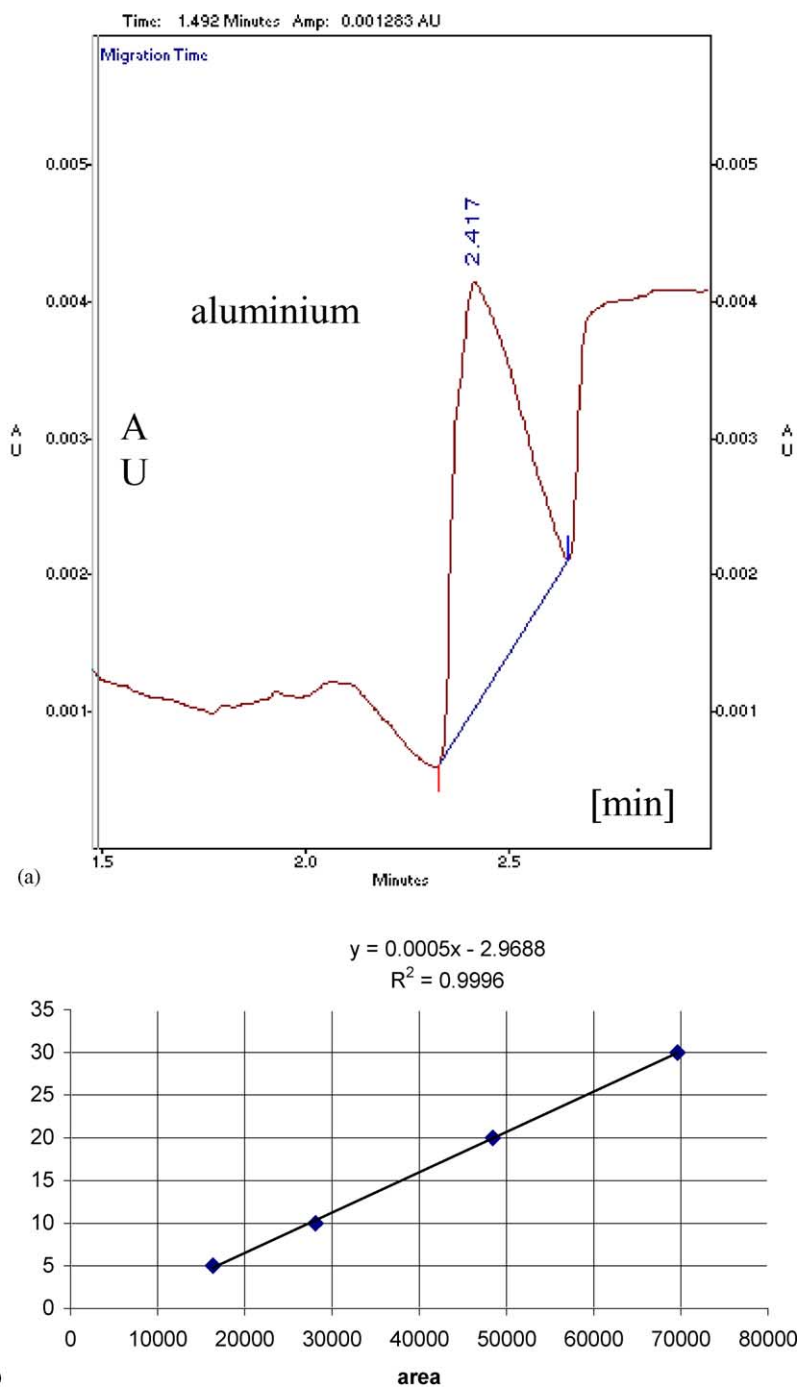


Fig. 3. (a) Electropherogram of aluminium in process sample. (b) Calibration of aluminium concentration with peak area. Range 5–30 mg/l. Electrolyte solution: 9 mM pyridine 12 mM glycolic acid 5 mM 18-crown-6-ether (pH 3.6).

normal process control monitoring in real time. However, when the sampling site was near enough the site of reagent addition and the measurements could be on-line monitored with short analysis time, the knowledge about the feeding breaks were noticed earlier. Fig. 7 shows the concentration curve of aluminium, where two shut-downs of the chemical addition can be seen as pits in the graphical depiction.

3.5. Corrosion

The corrosive power of the chemical solution in the steel tank can be predicted by the following equation, which calculates the molar ratios of Na_2SO_4 , NaCl and $\text{Na}_2\text{S}_2\text{O}_3$ as:

$$\frac{n_{\text{Na}_2\text{SO}_4} + 1/2n_{\text{NaCl}}}{n_{\text{Na}_2\text{S}_2\text{O}_3}}$$

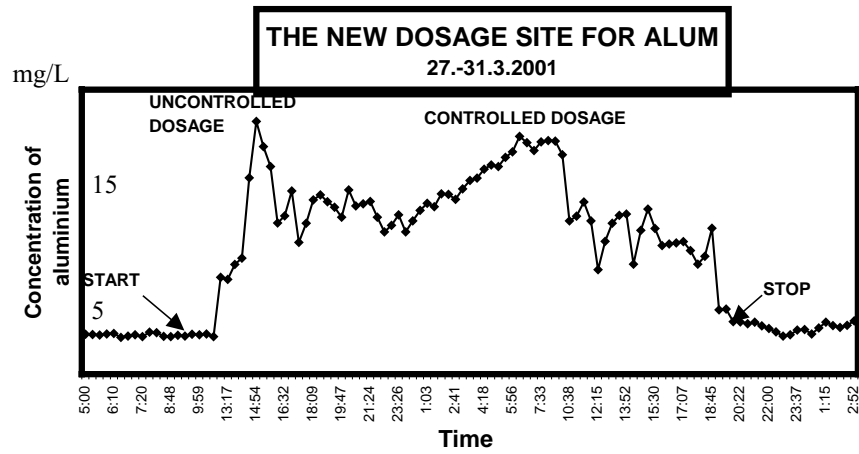


Fig. 4. Effect of dosage site of aluminium sulphate. Results obtained in on-line sampling over a 5-day period.

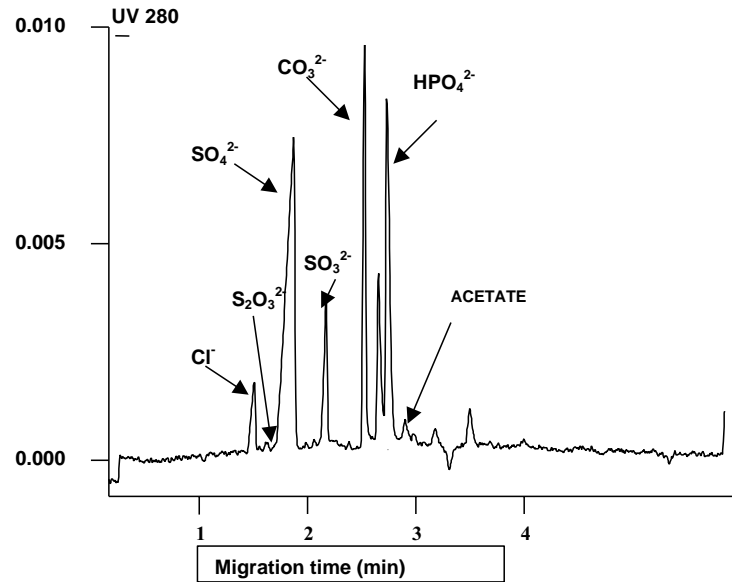


Fig. 5. Separation of anions in the process water of a paper machine. Buffer: Anions8.

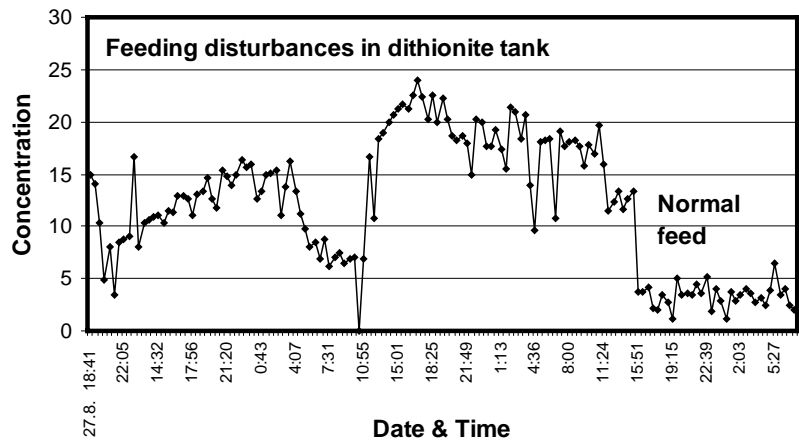


Fig. 6. Observed thiosulphate concentrations in a paper machine during the mill trial.

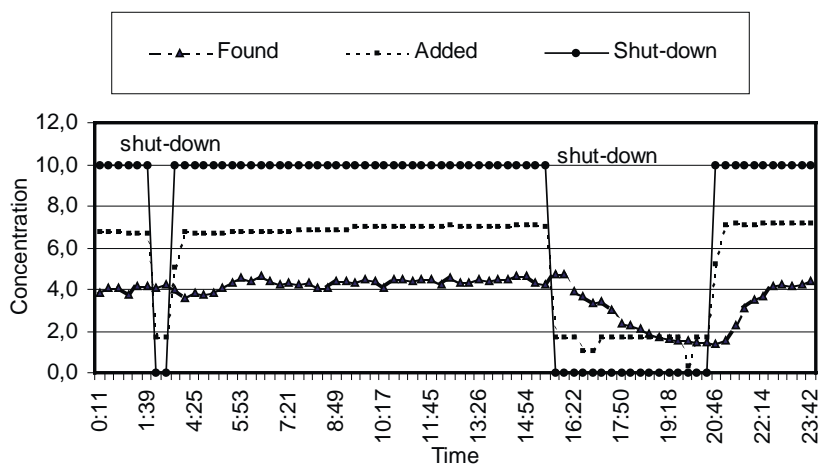


Fig. 7. Added and recovered aluminium and shut-downs during 1 day in the process water of a cardboard machine.

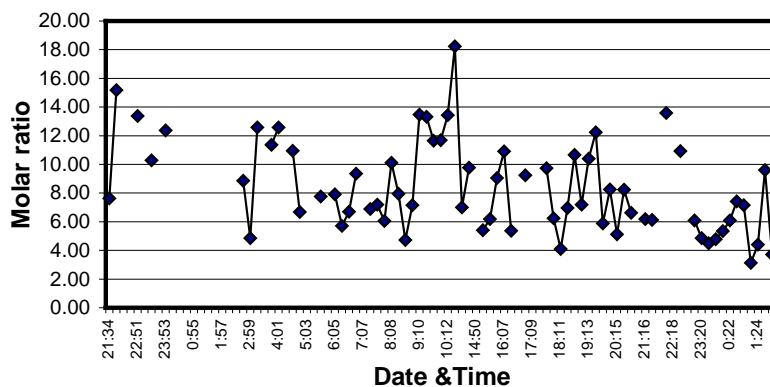


Fig. 8. Molar ratio of (sodium sulphate + 1/2 sodium chloride)/sodium thiosulphate in a paper machine during the mill trial.

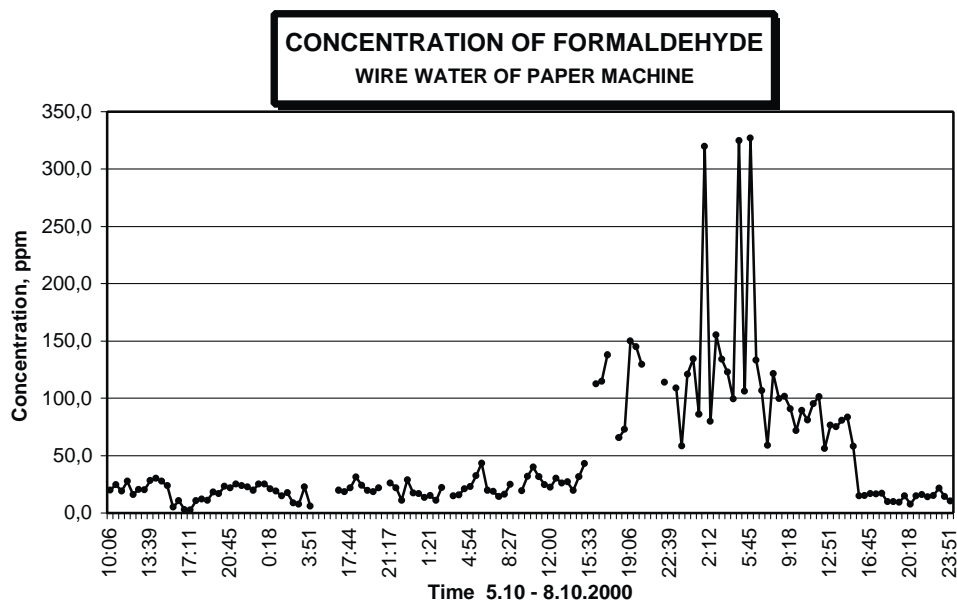


Fig. 9. The use of a biocide containing formaldehyde for the wire washing of a paper machine.

If the value of the ratio is between 10 and 20, there is a possibility of corrosion [5].

Fig. 8 shows the fluctuations of the molar ratio in the wire water of a paper machine obtained with our on-line CE measurements. The value of this ratio was generally below 10 in our tests and therefore no actual corrosion problems could be detected. Only, related to the addition of aluminium sulphate, the ratio was occasionally increased above the limit value.

3.6. Wire washing

Shut-downs may be planned or they can be expected. In every case they provide time to service machines. One of the services is wire washing. In the example a detergent containing formaldehyde is used for wire washing during shut-downs. The washing sequences during three days, when the CE instrument was on-line monitoring the service, can be seen as concentration peaks of formaldehyde in Fig. 9. During the three days the concentration of formaldehyde was generally low. High concentrations could be monitored during the washing period.

4. Conclusions

This study shows that CE is an excellent equipment for on-line monitoring of individual compounds in process waters at mills. The results can be used for estimating, e.g. chemical phenomena of the process waters, optimisation of dosage of chemicals, state of decomposition of dithionite and corrosion. The development of the CE on-line system required a batch-type feeding unit in the CE instrument to replenish the samples. The capillary electrophoresis system

could be run continuously periods of up to one week without stopping the measurements. The sampling could even be performed at intervals of only 15 min when 7–10 analytes were quantified. Different electrolyte systems were tested for sulphur compounds and the dosage of aluminium sulphate. Thiosulphate was used as the indicator for steel corrosion of the process water tanks. The degree of corrosion was calculated from the concentration ratios of sodium salts of sulphate, chloride and thiosulphate. Mainly, corrosion was not observed in our studies, except in one paper machine.

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