Determination of inorganic anions in papermaking waters by ion chromatography

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Abstract: A suppressed ion chromatography (IC) method for the determination of inorganic anions in process water from paperboard production was developed and validated. Common inorganic anions (Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) were detected in fresh and process water samples collected from a paperboard production system at 16 characteristic points. It was shown that the use of an IonPac®-AS14 column under isocratic conditions with $Na_2CO_3/NaHCO_3$ as the eluent and a suppression device proved to be a reliable analytical solution for the separation of the inorganic anions present in papermaking waters. This IC method is quite satisfactory concerning selectivity and sensitivity, and enables the determination of several inorganic anions over a wide concentration range. According to the obtained results, the total amount of analyzed inorganic anions was below 0.1 g/L, *i.e.*, below the critical value which may trigger operational problems in paper production.

Keywords: papermaking waters; ion chromatography; inorganic anions.

INTRODUCTION

A lot of efforts have been made to reduce the usage of fresh water and system closure in paper production.[1–5] The European Union Environmental Directive for Pulp and Paper Production commits producers to decrease fresh water consumption, which should be realized by water recirculation and water system closure.[6] In addition to the proven advantages, the closing up of the water system in paper production also brings different operational and product problems (chemical precipitation, low retention of fibers and fines, corrosion of equipment, microbiological growth, slime and odor inside mill and impurities in the final product).[7–11] These problems are mainly caused by increased concentrations of

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water-soluble compounds in the process water, *i.e.*, dissolved and colloidal organic and inorganic compounds. Monitoring the quality of the process water is the most popular and effective measure for controlling detrimental phenomena in paper production.[12–15]

It has been estimated that the number of analytical water measurements, mostly physical ones, to be made for one paper machine per day could increase to 1.500–2.000.[16] Usually, basic methods for water analysis include the measurement of summative parameters. Being simple and rapid, they are traditionally predominant in the determination of papermaking process waters and effluents. Particularly, on-line chemical measurements are focused on monitoring pH and conductivity. However, the results obtained provide only information about the chemical behavior of the individual ions and compounds. Therefore, there is a necessity for separation techniques, such as ion chromatography (IC) or capillary electrophoresis (CE), to verify the concentrations of individual ions.[17] These rapid, powerful, high-throughput and specific identification techniques, such as IC with suppressed conductivity detection, are required for on-line separation and simultaneous determination of ion species.[18]

IC Represents a universal analytical technique for the separation and quantitative determination of specific ion species. Complex mixtures of anions or cations can be separated to the level of specific ions and then quantified in a relatively short time.

The main applications of IC methods are in the determination of trace anions in ultra pure water, in the pharmaceutical industry, electronics, power plants, pulp and paper production, *etc*.[19] In modern paper production, the determination of the amount of anions in the process water is an important control parameter. The IC method can detect and quantify substances that cause color, smell and slime in the production process, as well as salts and other corrosive substances. These disturbing substances include volatile organic acids (acetic, formic, lactic and butyric) and inorganic salts present as anions: chloride, fluoride, sulfate, nitrate, *etc*.

The aim of this work was to develop and validate IC method for the determination of inorganic anions in process water of paperboard production. Fresh and process water samples from production system were analyzed by suppressed IC method. It was examined that, concerning selectivity and sensitivity, if combination of selected columns, eluent and operating parameters was well established, IC method was able to determine several inorganic anions in a wide concentration range.

EXPERIMENTAL

Water from one paperboard production system with a daily output of 180 t of coated and uncoated paperboard was analyzed. The main feedstock materials were waste paper (70 %), bleached and unbleached ground wood and softwood pulp (primary fibers), sludge, fillers,

$CaCO_3$, different additives, *etc*. Water was samples at 16 characteristic points during the commercial production of 400 g/m^2 paperboard with an average water consumption of 32 m^3/t. A schematic description of the production process in the examined paperboard mill with control points for water analysis is given in Fig. 1.

The produced paperboard was made up of seven layers, each formed on a separate former. The bottom layer (made of unsorted waste paper) was formed on formers 1 and 3. The inner layer was made of low-grade waste paper (on formers 4, 5 and 6) and the upper layer was made of high-grade waste paper (formers 7 and 8).
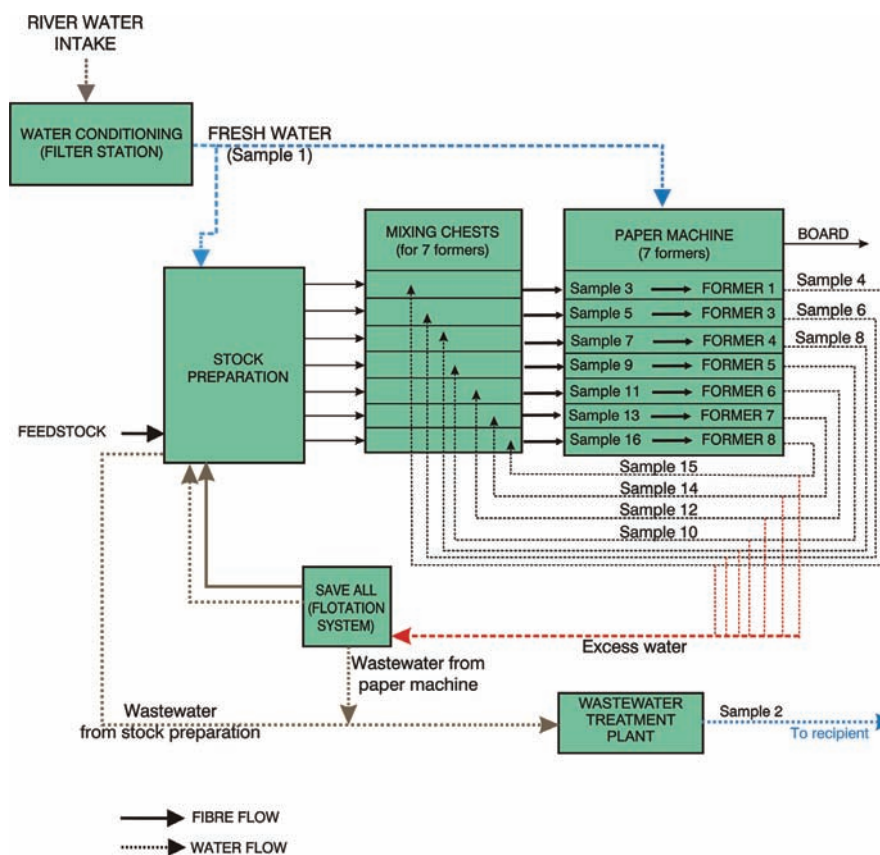

Fig. 1. Production process in a paperboard mill and the sampling points.

Instrumentation and operating conditions

Determination of inorganic anions by IC method was realized using a Dionex DX-300 ion chromatograph (Dionex, Sunnyvale, CA, USA). The instrument consists of an advanced gradient pump and a CDM-3 conductivity detector. The employed analytical separation column was a Dionex IonPac®-AS14 preceded by a Dionex IonPac®-AG14 guard column. Both columns were made of the same polymer resin for anion exchange. An Anion Self Regenerating Suppressor (ASRS ultra) was used. Dionex Peaknet ver. 5.1 software was employed for instrument control, data collection and processing. A Spectra-Physics model AS3500 autosampler was used for the direct programmed injection of samples.

TABLE I. Operating conditions for anion separation by suppressed IC method under isocratic conditions

Guard column	IonPac AG14 (4 mm×50 mm) anion exchange
Suppressor	ASRS-ULTRA (4 mm)
Mobile phase – Eluent	4.0 mM Na_2CO_3/1.0 mM $NaHCO_3$ (1:1)
Eluent flow rate	0.70 mL/min
Sample volume	20 μL
Injection technique	Direct
Detection	Suppressed conductivity
Full scale range	100 μS
Suppressor current	50 mA

Anion determination was realized under the optimal operating conditions presented in Table I. These parameters were determined by trial-and-error and were the same for all measurements of the water samples from the paper production system.

Separation and detection of anions were performed at room temperature and lasted for about 17 min for each sample.

Chemical reagents, standard solutions and eluent

All chemicals for the preparation of standard solutions and the eluent were of analytical--reagent grade and were dissolved in deionized (milli Q) water with a specific resistance of 18.2 MΩ cm. The stock standard solutions were stored at 4 °C. Standard working solutions of different concentrations were prepared by diluting the stock solutions with deionized water. Fresh working eluent was prepared daily, filtered through a 0.2 µm pore size membrane filter (Millipore, USA) and degassed before use. All standard solutions for calibration were stored in polyethylene containers.

Samples

Process water samples were collected *in situ* at selected control points in the production system. All samples were handled carefully and analyzed in the chemical laboratory as quickly as possible. Water samples with a higher turbidity (from headboxes and whitewater samples) were analyzed after removal of the suspended solids using a laboratory centrifuge (1500 min^{-1}, 30 min). All samples were filtered through a 0.2 µm membrane filter (Millipore, USA) just before injection.

RESULTS AND DISCUSSION

Common inorganic anions (Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) were identified and quantified applying the IC method under the operating conditions shown in Table I.

All the studied anions were determined in one chromatographic run. The identification and quantification of each anion were realized from the retention time and peak area. A typical chromatogram of a water sample is presented in Fig. 2.

The chromatographic parameters for the detected anions are presented in Table II. The recovery (*R*) and the relative standard deviation (*RSD*) of the peak area for spiked samples are given in Table III.
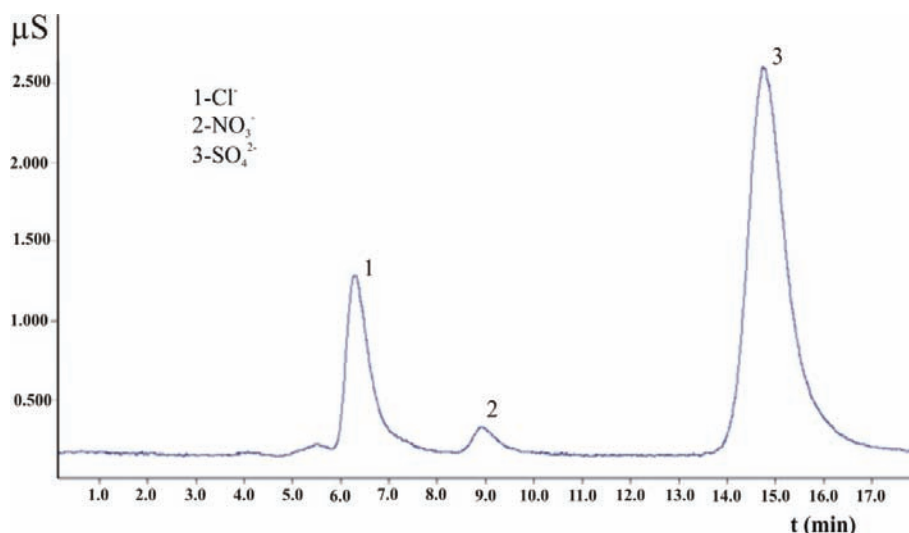
Fig. 2. Chromatogram of whitewater from former 8 (sample 15).

Table II confirms that the calibration lines obtained by the selected IC method (using the operating parameters presented in Table I) are linear with a correlation coefficient over 0.999 (except for phosphate) over the whole working concentration range. The calculated values for parameter a are much higher than is usual (for a calibration line which starts at the [0,0] coordinates). This can be explained by relatively large peak areas in the chromatograms.

TABLE II. Chromatography parameters for the detected anions: t_R – retention time; a and b – parameters for the calibration curve ($y = a + bx$, y – peak area, x – concentration); r – correlation coefficient

Anion	t_R / min	$-a \times 10^{-4}$ Area unit	$b \times 10^{-4}$ Area unit L mg^{-1}	r
Cl^-	6.28	2.1528	2.2003	0.9993
NO_3^-	8.88	1.8996	1.1261	0.9996
PO_4^{3-}	12.8	1.4429	1.4704	0.9987
SO_4^{2-}	14.6	9.2543	1.5833	0.9995

TABLE III. Recovery (R) and relative standard deviation (RSD) of the peak area for spiked water samples

Anion	R / %	RSD / %
Cl^-	102	2.4
NO_3^-	103	2.7
PO_4^{3-}	97	3.2
SO_4^{2-}	101	2.0

The previously developed and validated IC method was used as a control analytical tool for the analysis of water samples taken from the production pro-

cess. Sixteen different samples of process and waste water were prepared and injected into the chromatograph with $Na_2CO_3/NaHCO_3$ as the mobile phase. The concentrations of the commonly detected anions in the investigated water samples are presented in Table IV, while the descriptive statistics and reproducibility data (*RSD*) of the peak areas for the target inorganic anions in representative samples are given in Table V.

TABLE IV. Mean concentration values of the detected anions calculated from the peak areas (5 injections for each sample)

Sampling point/water type	Concentration, mg/L[a]			
	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Filter station (fresh water)	6.49	3.85	<0.05	35.5
Effluent to recipient	10.61	<0.01	<0.05	54.5
Headbox to former 1	11.33	<0.01	1.31	52.0
Whitewater from former 1	12.11	<0.01	<0.05	57.2
Headbox to former 3	7.61	<0.01	2.81	34.2
Whitewater from former 3	13.64	<0.01	4.53	64.4
Headbox to former 4	15.32	<0.01	3.91	67.3
Whitewater from former 4	14.63	0.14	1.90	65.4
Headbox to former 5	16.44	<0.01	3.25	76.9
Whitewater from former 5	14.02	<0.01	3.91	64.4
Headbox to former 6	15.21	<0.01	8.46	70.3
Whitewater from former 6	17.84	0.06	3.41	79.2
Headbox to former 7	8.85	2.10	<0.05	51.5
Whitewater from former 7	9.75	1.62	<0.05	51.7
Whitewater from former 8	8.10	2.69	<0.05	48.0
Headbox to former 8	8.08	2.68	<0.05	108.1

[a]Uncertainty of measurement presents 95 % of significance level: 0.05 mg/L for Cl^-, 0.01 mg/L for NO_3^- and PO_4^{3-} and 0.1 mg/L for SO_4^{2-}

TABLE V. Descriptive statistics and *repeatability* data (*RSD*) of the peak area for the target inorganic anions in samples 1, 2, 8 and 12 ($n = 5$)

Anion	Sample 1 (Filter station/fresh water)				Sample 2 (Effluent to recipient)				Sample 8 (Whitewater from former 4)				Sample 12 (Whitewater from former 6)			
	Concentration mg/L			*RSD* %	Concentration mg/L			*RSD* %	Concentration mg/L			*RSD* %	Concentration mg/L			*RSD* %
	Min	Max	Mean		Min	Max	Mean		Min	Max	Mean		Min	Max	Mean	
Cl^-	6.2	6.90	6.5	3.2	9.2	11.8	10.6	5.5	12.9	15.8	14.6	7.3	16.6	18.3	17.8	7.8
NO_3^-	3.7	4.0	3.8	3.0	nd[a]	nd	–	–	0.06	0.24	0.14	7.8	0.04	0.10	0.06	8.5
PO_4^{3-}	n.d.	n.d.	–	–	nd	nd	–	–	1.5	2.5	1.9	7.1	3.0	3.8	3.4	8.2
SO_4^{2-}	34.6	36.7	35.5	2.3	52.9	55.8	54.5	4.4	63.8	66.7	65.4	6.0	78.4	80.1	79.2	6.2

[a]Not detectable

Chlorides and sulfates were detected in all the water samples, which can be explained by the addition of these chemicals as retention aids into the production

process. Comparing the contents of Cl^- and SO_4^{2-} in the fresh water and the effluent (samples 1 and 2), no great difference could be observed. Furthermore, it shows that a larger amount of the added chemicals was settled down with the fibers and kept in the paper, which indicates a highly efficient retention of the fibers. Comparing the contents of Cl^- and SO_4^{2-} in water samples from the headboxes of different formers, the highest concentrations were recorded for formers 4–6 (and 8 for sulfates). These formers are used to make the inner layers of paperboards, except former 8 which is used for the upper layers. The middle layer is made up of the lowest quality recycled paper with the shortest fibers. On these formers, the retention is not so intense, which demands addition of retention aids. This is also the reason for the higher concentrations of residual (dissolved) Cl^- and SO_4^{2-} anions in the whitewaters from formers 4–6 and 8 (for sulfates).

Nitrates and phosphates were detected in 7 of 16 samples (resp. 9 of 16 samples), and their concentrations were below 3.85 (NO_3^-) and 8.46 (PO_4^{3-}) mg/L, respectively. It is important to perceive that neither NO_3^- nor PO_4^{3-} were detected in sample 2 (effluent to recipient). These anions, when present in higher concentrations, might result in higher values of total nitrogen and phosphorus in the paper production effluent, which is limited by the EU Environmental Directive for Pulp and Paper Production.

In addition to the anions presented in Table IV, Br^-, NO_2^- and F^- were also analyzed but they were not detected, because their concentrations were below 0.01 mg/L. Nitrites are unstable at higher temperatures (about 50 °C, which is a characteristic of process water), which might be the reason why they were not detected. Also, nitrites can hardly be detected in the presence of organic acids, which are predominantly present in papermaking waters.

Reproducibility tests were based on five injections for each water sample. The reproducibility data for the peak areas, obtained using the operation parameters described in Table I, were statistically evaluated from the relative standard deviation (*RSD*) and are presented in Table V.

All *RSD* values of the peak areas for the target anions (presented in Table V) were less than 9 %. Comparing the *RSD* values for examined samples, it can be seen that the best results of the precision of the measurement (lowest *RSD* value) were recorded for sample 1 – fresh water from the filter station. This can be explained by the low presence of interfering substances in the fresh water, which were previously removed in the clarification process. Comparing *RSD* values for the detected anions, it can be noticed that the highest precision in all the samples (lowest *RSD* value) was recorded for SO_4^{2-}. This fact might be explained by the highest concentrations (and the largest peak areas) of sulfates in all the analyzed water samples.

The obtained results show that the use of an IonPac-AS14 column under isocratic conditions with Na_2CO_3/$NaHCO_3$ solution as the eluent together with a

suppression device provides for good separation of inorganic anions from paper-making waters. All the detected anions were eluted in less than 17 min and their peaks were well separated (Fig. 2). It is a suitable method for the determination of anions in the concentration range from 0.1 to 100 mg/L by direct sample injection and it can be used for a routine analysis of papermaking waters. Direct injection does not require any previous pre-concentration of the samples and presents a simple but reliable method for ion analysis.

The results given in Table IV confirm that the total amount of analyzed inorganic anions (except for sample 16 – headbox to former 8) was below 0.1 g/L, *i.e.*, far below the critical value, which may induce operational problems caused by the anions present. However, increased concentration of sulfates in sample 16, which raised up the total amount of inorganic anions to 0.119 g/L, had not caused any operational problem. According to practical experiences, further closing of the water system with increased recirculation, as well as the usage of recycled fibers instead of cellulose may cause an increase in the concentration of detrimental anions, which should be controlled.[12]

As expected, the highest concentration of anions was recorded for sulphates, which are the main cause of process equipment corrosion. To determine inorganic anions such as Br^-, NO_2^- and F^-, which could not be detected in the present study, further investigation may include modifications in the eluent, eluent flow rate, stationary phase or column temperature.

Also, the analysis of papermaking process water should include organic acids (lactic, acetic, formic and butyric acid). These organic acids are the metabolic products of microorganism population growth in the closed water system of paper production. Increased concentration of volatile organic acids may cause a decrease in production efficiency, corrosion problems, as well as the appearance smell and slime in paper mills.

CONCLUSIONS

Inorganic anions in papermaking waters were successfully determined by a suppressed IC technique using an anion-exchange separation column, Na_2CO_3/$NaHCO_3$ solution as the eluent, and a suppression device. Major inorganic anions, usually present in papermaking waters (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}), were efficiently separated and quantified. However, some inorganic anions (Br^-, NO_2^- and F^-) could not be detected because of their lower concentrations (below 0.01 mg/L), which remains to be solved in further examinations. The total amount of detected inorganic anions was below 0.1 g/L, which is the critical value for triggering operational problems in paper production. The highest concentration of anions was recorded for sulfates, which are the main cause of corrosion of process equipment.

Further closure of the water system with increased recirculation, as well as an enhanced usage of recycled fibers as a raw material, will affect an increase in the concentration of detrimental anions. Monitoring of these anions by the IC method should be an integral part of modern paper production systems, in order to prevent operational and product problems.

ИЗВОД

ОДРЕЂИВАЊЕ НЕОРГАНСКИХ АНЈОНА У ВОДАМА ИЗ ПАПИРНЕ ИНДУСТРИЈЕ МЕТОДОМ ЈОНСКЕ ХРОМАТОГРАФИЈЕ

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Одређивање неорганских анјона у водама кружног тока у производњи папира вршено је методом супресивне јонске хроматографије (IC). Најважнији неоргански анјони (Cl⁻, NO_3^-, PO_4^{3-} и SO_4^{2-}) квантитативно су одређени у 16 узорака свеже и процесне воде једног система за производњу картона. Добијени резултати указују на то да употреба IonPac-AS14 сепарационе колоне у изократским условима са елуентом Na_2CO_3/$NaHCO_3$ и саморегенеришућим анјонским супресором (ASRS) представља поуздану IC методу за раздвајање неорганских анјона у процесним водама папирне индустрије. Резултати су показали да је изабрана IC метода сасвим задовољавајућа у погледу селективности, осетљивости и прецизности, и да је била идеална за одређивање анјона у опсегу концентрација mg/L. На основу резултата, укупна концентрација испитиваних неорганских анјона је испод 0,1 g/L, што представља критичну вредност за појаву оперативних проблема у системима за производњу папира.

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