ION CHROMATOGRAPHY – A USEFUL NON-DESTRUCTIVE TOOL FOR MONITORING AQUEOUS CONSERVATION TREATMENTS OF CELLULOSE MATERIALS

Kirsi Perkiömäki, Ulla Knuutinen, Taina Leppilahti, Päivi Ukkonen
EVTEK University of Applied Sciences, EVTEK Institute of Art and Design, Conservation
Department, Lummetie 2 b, 01300 Vantaa, Finland
Author: kirsi.perkiomaki@evtek.fi, Fax: +358 9 8237489

ABSTRACT

The IC has not been widely applied in conservation research, but it seems to be a very useful tool for optimizing and controlling aqueous treatment processes. IC analyses offered a novel non-destructive tool for studying aqueous washing and neutralization conservation treatments, because samples can be taken direct from treatment solutions. Ion chromatography (IC) method was used for analyzing washing solutions of cellulose paper and textile samples.

Metrohm 761 Compact HPIC device, coupled with the chemical suppressor was used for ion chromatography (IC) analyses. As a pre-treatment, samples were filtered and run through Dialysis (754 IC) unit, which separates high molecular (cellulose) substances from solutions. Standard calibration was performed for fluoride, chloride, nitrite, bromide, nitrate and sulphate anions and sodium, ammonium, potassium and magnesium cations with five concentrations between 0,25 mg/l and 20 mg/l. For acetate and formiate, 5 mg/l reference standard was used for defining the retention times of these anions.

For the IC analyses, samples were taken from the washing and Ca2+ and Mg2+ contained deacidifying solutions of the old "rag" paper book from the year 1831. Also washing solutions of two linen and three cotton, cellulose textiles, cassocks lining cloths or pillowcases, were studied with the IC. The washing and deacidifying processes were controlled also with pH measurements.

Results of IC analyses of anions gave direct information of the amount of water soluble sulphates, chlorides, nitrates and phosphates. IC analyses of washing solutions showed that variable amount of nitrates, phosphates and sulphates were coming out of cellulose samples within 15 minutes. There was not any more increase in amount of anions if the washing process was continued up to 30 minutes. Further, the water soluble degradation products of cellulose, acetates and formiates, were found in washing solutions. The IC analyses of Ca^{2+} and Mg^{2+} cations were succesfully applied for monitoring the validity of treatment solutions in deacidifying processes as well as for finding out the amount of neutralization agents binding to paper cellulose fibers.

INTRODUCTION

In the conservation processes of cellulose materials, aqueous treatments consist of cleaning or washing with water, deacidification and neutralization. The effectiveness of these processes has so far been studied mainly by destructive methods analysing changes in cellulose material properties and by monitoring pH.[1-6] This paper shows that IC (Ion Chromatography) analyses offer a useful non-destructive tool for studying water based conservation treatments. The method is non-destructive, because samples can be taken directly from aqueous solutions.

The aim of the IC studies was to continue previous research work for optimizing and controlling washing and deacidification processes of paper and textile cellulosic materials[7] Washing and treating solutions were analysed with the ion chromatography in order to detect water soluble anions: sulphates, chlorides, nitrates and phosphates from old "rag" paper and from new paper. The cation analyses were used for monitoring deacidifying solutions and to find out, how alkalies, Ca^{2+} and Mg^{2+} bind to paper during the neutralization process.

Some washing processes of cotton and linen textiles were also monitored by anionic analyses. With textile samples, interest concentrated on anions to be washed away from textile fibres. In

addition to sulphates, chlorides, nitrates and phosphates, the IC was used to study acetates and formiates, the degradation products of textile cellulose fibres.

All the washing and deacidifying processes were controlled with pH measurements. Further more, several different analytical methods: XRD, SEM-EDS, CIE *L*a*b** colour measurements were made to analyse paper samples. This poster/paper presents the results of the IC studies. Other research results are summarized elsewhere.[8]

EXPERIMENTAL
Chromatographic System
Ion-Exchange Chromatography (HPIC, High Performance Ion Chromatography) is a liquid chromatography technique, which is based on ion-exchange processes occurring between the mobile phase and ion-exchange groups bonded to the support material.[9] It is used for the separation of both inorganic and organic cations and anions. The IC has good sensitivity: the detection limits for simple inorganic anions and cations are about 10 μg/l. The Metrohm 761 Compact HPIC device, coupled with chemical suppressor, was used to analyse both anionic and cationic samples. As a pre-treatment, samples which were taken from washing and deacidifying solutions, were treated with Dialysis (754 IC) unit, which separated high molecular (cellulose) substances from solutions.

Anionic analyses were performed with Metrosep A Supp 5 (6.1006.530) column, size 4.0 x 250 mm and particle size 5.0 μm. Eluent was 3.2 mmol/l Na_2CO_3 / 1.0 mmol/ NaOH (pH ~ 10) with chemical suppression with 0,05 M H_2SO_4. Conditions for anionic analyses were: Injection volume 20.0 μl, flow rate 0.7 ml/min, temperature 20.0 ºC and pressure 13.2. MPa. Standard calibration was performed for fluoride, chloride, nitrite, bromide, nitrate and sulphate anions with five concentrations between 0,25 mg/l and 20 mg/l. For analyses of textile samples also formiates and acetates were confirmed with 5 mg/l standard. In addition, checking standard of 5 or 10 mg/l was run between the samples.

For the cationic analyses Metrosep C 2 (6.1010.230) column, size 4.0 x 250 mm and particle size 7.0 μm was used. Eluent was 4 mmol/l tartaric acid and 0,75 mmol/l dipicolinic acid. Conditions for cationic analyses were: injection volume 20.0 μl, flow rate 1,2 ml/min, temperature 20.0 ºC and pressure 13.2. MPa. Standard calibration was performed for sodium, ammonium, calcium and magnesium cations with same concentrations as in anionic analyses.

Reagents and Samples
Old "rag" paper samples, mainly pure flax fibres, were taken from the margins of an old book, printed 1831. New paper was Whatman filter paper 1,90 mm Dia (Cat No 1001090). All treatment solutions: purified (Millipore Elix) water, 0,02 M $Ca(OH)_2$ and 0,04 M $Mg(HCO_3)_2$ –solutions were analysed with ion chromatography to make sure that the concentrations were correct. References indicated that bubbling CO_2 gas through solution will improve magnesium´s solubility[10,11]. Two batches of 0,04 M $Mg(HCO_3)_2$ –solutions were prepared. First solution was filtered before bubbling; in second solution precipitation was let to stay in solution during bubbling. Washing solutions from both new and old paper were analysed in order to find out, which ions had moved from paper to water. Papers (1 gram each) were washed with 100 g of distilled water for 30 minutes. For the IC analysis liquid samples were taken after 15 and 30 minutes. Papers were dried and after that neutralization treatments were performed. Because solutions (especially those were old paper was used) were cloudy, samples were filtered with Whatman 0,54 μm filters, diluted and dialysed before analysing, in order to remove cellulose and other colloid particles. All the samples were prepared and analysed in duplicate.

Textile samples were two linen and three cotton cellulose textiles, chasuble lining cloths or pillowcases. For washing textiles, 100 millilitres of pure Milli-Q water per 1 gram textile sample was used. Treating temperature was 20 ° C and time one hour. Samples were taken from washing solutions for the IC analyses every 15 minutes.

A common method for controlling treatments is the determination of pH.[6,12] PH measurements were performed before and after washings. For papers measurements were repeated also before and after neutralization treatments. Measurements were done with surface electrode, calibrated with pH 4,00 and pH 7,00 solutions. For papers pH measurements were also done as extraction according to TAPPI 509 om-02 standard[12]. 0,5 grams of paper samples were weighted in beaker and 10 milliliters of distilled water were added. Sample was stirred with magnetic stirrer until it was fully wet. After this 25 milliliters of distilled water were added and stirred well for ten minutes. Samples were let to stand for one hour, stirred and pH were measured. Samples were prepared in duplicate. Ion chromatography analyses were performed for all the washing and treating solutions to confirm their purity.

RESULTS (IC)

Cation analyses (Table 1.) of deacidifying solution 0,02 M $Ca(OH)_2$ proved the solution to contain ca. 826,55 mg of calcium per litre, which converted to concentration equals 0,0206 M solution. Cation analyses of 0,04 M $Mg(HCO_3)_2$ –solutions showed differences. First solution showed only a few milligrams of magnesium, from second solution the amount of magnesium was found to be ca. 944 mg/l and concentration 0,039 M. The concentration of second solution was correct for neutralization treatments. The IC analysis revealed the mistake of preparing the first magnesium solution. This emphasizes the fact that the concentrations of treating solutions should be studied before using them for conservation treatments. Analyses of cations also showed that concentration of calcium diminished from 0,02 M to 0,018 M during treatments, which indicates that some Ca^{2+} ions moved to the paper. Analyses of magnesium solutions did not follow the same trend. This phenomenon could also be proved with SEM- EDS and XRD studies[8].

Sample	Na^+ mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l	Conc. in original sample / M
0,02 M $Ca(OH)_2$, dil 1:50	-	16,67	-	0,021
0,02 M $Ca(OH)_2$, dil 1:50	-	16,40	-	0,020
Whatman treated w. $Ca(OH)_2$, dil 1:50	-	14,12	-	0,018
Whatman treated w. $Ca(OH)_2$, dil 1:50	-	14,05	-	0,018
Old paper treated w. $Ca(OH)_2$, dil 1:50	< Cal	14,32	-	0,018
Old paper treated w. $Ca(OH)_2$, dil 1:50	< Cal	14,82	-	0,018
0,04 M Mg-sol, 1.st port., dil 1:50	< Cal	-	0,48	
0,04 M $Mg(HCO_3)_2$ 2.nd port.	< Cal	0,50	18,98	0,039
0,04 M $Mg(HCO_3)_2$ 2.nd port.	< Cal	-	18,80	0,039
0,04 M $Mg(HCO_3)_2$ 2.nd port.	< Cal	-	18,89	0,039
Whatman treated w. $Mg(HCO_3)_2$, dil 1:50	< Cal	0,29	20,21	0,042
Whatman treated w. $Mg(HCO_3)_2$, dil 1:50	< Cal	0,36	20,23	0,042
Old paper treated w. $Mg(HCO_3)_2$, dil 1:50	-	0,60	19,86	0,041
Old paper treated w. $Mg(HCO_3)_2$, dil 1:50	-	0,65	19,59	0,040

Table 1. The results of cation analyses of papers.

In Table 2 are shown results of anion analyses of papers. Millipore water showed no traces of any anions. Sulphates appeared to be the largest group of anions in the paper washing

solutions. Further more, the IC analyses showed that some chlorides, nitrates and phosphates were washed out from old paper´s cellulose fibres. IC chromatograms showed also traces of compounds that probably were acetates and formiates and these compounds were further studied from textile washing solutions.

Sample	F^- mg/l	Cl^- mg/l	NO_3^{2-} mg/l	PO_3 mg/l	SO_4 mg/l
Milli-Q-water	-	-	-	-	-
Whatman washed w. H_2O 15 min	< Cal	0,63	0,38	-	0,5
Whatman washed w. H_2O 15 min, dil 1:2	< Cal	0,72	0,39	-	0,55
Old paper washed w. H_2O 15 min	< Cal	3,31	3,01	1,62	5,77
Old paper washed w. H_2O 15 min, dil. 1:2	< Cal	2,56	2,91	1,44	5,69
Whatman washed w. H_2O 30 min 1/2	< Cal	0,49	0,27	-	0,4
Whatman washed w. H_2O 30 min 2/2	< Cal	0,46	0,27	-	0,4
Old paper washed w. H_2O 30 min, dil. 1:2	< Cal	2,42	2,37	1,44	5,26
Old paper washed w. H_2O 30 min, dil. 1:2	< Cal	2,40	2,39	1,41	5,31

Table 2. The results of anion analyses of papers. From paper samples mainly chlorides, nitrates, phosphates and sulphates were washed away.

In Table 3 are results of anion analyses of textiles. Ion exchanged water (from Tupulatäkki) used for washing one textile sample, contained small amounts of fluorides and chlorides. The IC analyses of washing solutions showed that variable amount of chlorides, nitrates, phosphates and sulphates were coming out of cellulose fibers within 15 minutes. There was no more increase in amount of anions if the washing process was continued up to 30 minutes. It seems that sulphates might correlate with acidity in cellulose materials, because in cellulose samples pH values increased along with washing process. Sulphur (also nitrogen) compounds very likely originate from pollutants. In cellulose materials they form acids that can promote acidic hydrolysis.[14] It is clear that IC analyses offer a valuable tool for analysing the extraction of acidic pollutants.

Sample	F^- mg/l	CH_3COO^- mg/l	COO^- mg/l	Cl^- mg/l	NO_3^{2-} mg/l	PO_3 mg/l	SO_4 mg/l
Standard 5 mg/l	4,249	-	-	4,69	4,77	4,59	4,72
Water sample EVTEK Milli-Q	-	-	-	-	-	-	-
Water sample tupulatäkki	< Cal	-	-	0,22	-	-	-
Pillowcase, linen, 15 min, 1/2	< Cal	0,64	1,64	1,83	0,24	-	2,25
Pillowcase, linen, 30 min 2/2	< Cal	0,68	1,67	2,16	0,23	-	2,35
Chasuble lining cloth, linen, 15 min 1/2	< Cal	-	0,33	1,29	0,63	0,79	13,74
Chasuble lining cloth, linen, 30 min 2/2	< Cal	-	0,33	1,15	0,63	0,90	14,00
Stole lining, cotton satin, 15 min 1/2	< Cal	0,21	0,27	0,49	-	-	-
Stole lining, cotton satin, 30 min 2/2	< Cal	0,17	0,27	0,43	-	-	-
Pillowcase, cotton, 15 min 1/2	< Cal	-	0,30	1,48	-	-	0,65
Pillowcase, cotton, 30 min 2/2	< Cal		0,30	1,57	< Cal	-	0,65
Chasuble lining cloth, cotton,15 min, 1/2	0,43	-	0,17	8,46	4,85	3,39	4,68
Chasuble lining cloth, cotton,30 min, 2/2	< Cal	-	0,19	8,50	4,88	2,89	4,80

Table 3. Results of anion analyses of textiles. Samples taken after 15 and 30 minutes of washing.

In the analysis of paper washing solutions, the water soluble degradation products of cellulose, acetates and formiates, were found in trace amounts. Based on these results acetates and formiates were also assumed to be present in textile washings. Concentrations remained mainly under 1 mg/l, except with first sample, where concentrations of formiates were on

average 1,65 mg/l (Table 3). Because concentrations of acetates and formiates are low, further research and calibrations with smaller standards are necessary.

CONCLUSIONS

The results showed that the Ion Chromatography is very useful non-destructive tool for studying aqueous conservation treatments of paper and textile cellulose materials. The IC analyses of Ca^{2+} and Mg^{2+} cations were successfully applied for monitoring the validity of treatment solutions in deacidifying processes as well as for determining the amount of neutralization agents binding to paper cellulose fibers.

The IC analyses of anions gave direct information of the amount of water soluble anions. IC analyses of washing solutions proved out that variable amount of sulphates and nitrates, which might have connection to acidic pollutants, were coming out of paper and textile cellulose samples within the first 15 minutes. This information is important for optimizing the length of washing processes of papers and textiles, which contain cellulose fibers. Further more, the IC anionic analyses can reveal water soluble degradation products of cellulose fibers.

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