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A new method for the analysis of soluble and insoluble oxalate in pulp and paper matrices

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ABSTRACT

A novel method has been developed for determining soluble and insoluble forms of oxalate in pulp and paper samples by ion chromatography. Methanesulphonic acid is used to dissolve insoluble oxalate, and total oxalate is then determined by ion chromatography with suppressed conductivity detection. Soluble oxalate is determined directly by ion chromatography, without prior chemical treatment. Insoluble oxalate is obtained by difference. The method was validated and applied to samples of pulp, process liquors, filtrates, and scale deposits from kraft mills. In kraft mills, considerably higher levels of oxalate were found in the Eop samples compared to those in the brownstock and D_0 samples. In both brownstock and Eop samples, oxalate was mainly present in soluble form, whereas the D_0-stage contained relatively higher levels of insoluble oxalate. The new method will allow for the evaluation of the effect of process variables on the sources and forms of oxalate in mills, and to assess the effectiveness of various strategies to control oxalate scale deposition.

KEYWORDS

Oxalate, soluble, insoluble, methanesulphonic acid, ion chromatography, pulp and paper

1. INTRODUCTION

Oxalic acid and calcium oxalate are naturally present in both the wood and the bark of plants, including most species of trees [1-6]. While both substances are released from the wood during the various stages of pulp and paper manufacturing, the vast majority of oxalic acid and calcium oxalate present in pulp and paper mills is formed in the pulping and bleaching stages in kraft, primarily via the oxidation of lignin and to a lesser extent carbohydrates [6-10].

The two acid forms ($H_2C_2O_4$ and $HC_2O_4^-$; $pK_1 = 1.3$, $pK_2 = 4.3$) and the fully ionized form of oxalic acid (oxalate, $C_2O_4^{2-}$ or Ox^{2-}) are very soluble in water. On the other hand, calcium oxalate (CaC_2O_4 or CaOx) is known to form three hydrates (mono-, di- and trihydrate), all of which are only sparingly soluble in water. Under conditions prevailing in pulp and paper mills, calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$ or COM) is the most thermodynamically stable, and thus the major form of CaOx present in process samples and in oxalate-based scale deposits. As noted earlier, the majority of COM found in mills forms *in-situ* via the reaction between calcium ions originating primarily from the water and wood supplies, and oxalic acid released from the wood and that which is formed in the pulping and bleaching stages. A number of factors, such as temperature, pH, the presence of organic substances and certain metal ions as well as the ionic strength play significant roles in the solubility of calcium oxalate in model aqueous systems and mill process streams [11-27].

System closure (reduction of fresh water use) is a major goal in most pulp and paper

mills. However, its implementation leads to significant increases of dissolved and

colloidal substances, including calcium and oxalate ions [19]. This in turn results severe

deposition of COM, which forms and accumulates in several locations, such as on the

surface of washer wires, within storage tanks, evaporators, pipes, valves, and on

papermachine wires and papermachine felts [28]. Such deposition leads to upsets in mill

process operations, and causes frequent shutdowns specifically for the purpose of

descaling equipment. The shutdowns result in significant economic losses in terms of

lost production and cleaning costs for the affected mills. Despite considerable published

work on calcium oxalate formation and scaling, knowledge of the factors that aggravate

scaling under mill conditions is still incomplete. In addition, there is no reliable and

simple laboratory method available for predicting the propensity for CaOx scale

formation or for assessing the efficacy of scale control additives and strategies in

reducing CaOx scale formation in mills. Availability of reliable methods for measuring

the soluble and, in particular the insoluble forms of oxalate, is a prerequisite to better

understanding and control of calcium oxalate scale deposition more effectively. In the

case of pulp and paper applications, only a few analytical methods have been published

to date [6, 29, 30]. In some cases, the methods involve a lengthy sample preparation step,

may be time consuming or they may not have been validated. The current work reports

on the development of a new and reliable method for measuring soluble and insoluble

forms of oxalate in pulp and paper matrices; the method is based on ion chromatography

(IC).

2. EXPERIMENTAL

2.1 Instrumentation

All IC analyses were performed with a DX-600 ion chromatographic system (Dionex, Sunnyvale, CA, USA) consisting of a gradient pump (GP 50), a chromatographic module (LC 20), which housed a Rheodyne injection valve fitted with a 25 μL sample loop; separation columns; an ASRS ULTRA-II anion suppressor (4 mm); a thermostated conductivity cell, which was controlled by an ED 50 module; and an AS 40 autosampler, into which all standards and samples are placed for injection into the IC.

2.2 Columns and separation conditions

Separations were performed with Dionex IonPac AG4 guard (4 x 50 mm) and IonPac AS4 analytical columns (4 x 250 mm) connected in series. An eluent comprised of 2.25 mM Na_2CO_3 and 2.8 mM $NaHCO_3$ was used for the separation of oxalate from other anions present in the samples and was delivered to the columns at a flow rate of 1.50 mL/min (nominal operating pressure ca. 750 psi). All separations were conducted at ambient room temperature (ca. 18-23 ºC). A Dionex in-line filter apparatus containing two 5μm filters was placed upstream from the inlet of the guard column to remove particulates from the flow stream.

A regenerant consisting of 25mM H_2SO_4 (prepared by dilution of standard 2M H_2SO_4 in Milli-Q water) was delivered to the suppressor at a flow rate of 4 mL/min (background conductivity ca. 17.5 μS). High purity He was used to pressurize the eluent and

regenerant reservoirs, and to actuate the sample injection valve. Instrument control and

data acquisition were performed using Chromeleon® software (version 6.5 SP-1, Dionex).

2.3   *Reagents*

Reagent grade sodium oxalate ($Na_2C_2O_4$), sodium carbonate, (Na_2CO_3), sodium hydrogen

carbonate, ($NaHCO_3$), calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), methanesulphonic acid

(CH_3SO_3H, MSA) and Amberlite IR-120 cation-exchange resin (H-form) were purchased

from Aldrich Chemical Company Inc. (Milwaukee, WI, USA). A combined five anion

standard solution containing chloride, nitrite, phosphate, nitrate and sulphate was

obtained from Dionex and diluted in water to prepare calibration standards. Several forms

of high purity calcium oxalate, including CaC_2O_4, $CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot 2H_2O$ were

used. High purity 18 MΩ water was obtained from a Millipore Milli-Q Plus water

purification system (Bedford, MA, USA) and used in all aspects of the study.

2.4   *Preparation of standards*

A stock standard solution containing 1000 mg/L $C_2O_4^{2-}$ was prepared by dissolving an

appropriate and accurately known mass of reagent grade $Na_2C_2O_4$ in 100 mL of Milli-Q

water. The solution was stable for at least six months when stored in the dark at room

temperature. Initially, dilute oxalate standards, with concentrations ranging between 0.1

and 25 mg/L, were prepared in water and in various concentrations of aqueous MSA

(0.25-7.5% v/v) to assess its effect on the separation of and detector response to oxalate.

Regardless of the solvent used for dilution, all standards were prepared fresh daily by

diluting aliquots of stock oxalate solution to volume with and without MSA added. A

series of six anion standard solutions ranging in concentration between 0.1 and 25 mg/L

of oxalate and containing, chloride, nitrite, phosphate, nitrate, sulphate and oxalate in

water were prepared by combining aliquots of Dionex standard five anion stock with the

oxalate stock in a volumetric flask followed by dilution to volume with water. Oxalate

and/or mixed standards were placed in autosampler tubes and injected into the IC, via the

autosampler, at the beginning and the end of each day to obtain calibration plots for

oxalate and the other anions mentioned above. Such plots were found to be linear for

oxalate and for the other anions studied, over the concentration range specified above,

and were used to determine the concentration of oxalate in a sample. A standard solution

of anions was injected after every fourth sample to verify the performance of the IC

system.

2.5   *Sample collection and storage*

Samples were collected from kraft mills: they included vat samples from the brownstock,

D_0- and Eop-stage washers. All samples were collected and stored in polypropylene

bottles and refrigerated (at $4^{o}C$) when not in use. The temperature and pH of each sample

were recorded at the time of sampling. The moisture content of wood chips, pulp and

pulp slurries were determined by thoroughly drying a small portion of each sample at 105

°C in a hot air oven for at least 6 hours. Wood chips were ground to a fine powder with

the aid of a Wiley mill.

2.6   *Analysis of total oxalate in pulp and paper samples*

The novel aspect of the reported entails using MSA to rapidly and completely dissolve insoluble forms of oxalate, which is mainly present as COM in the case of pulp and paper samples. MSA is a strong acid with a pKa value of -1.9 at 25°C, which forms soluble complexes with many metals [31, 32]. In addition, MSA has a relatively high boiling point, a low vapor pressure, does not produce volatile gases when exposed to moist air or when diluted in water, has low toxicity and is biodegradable [31]. In practical terms, this means that MSA can be handled and disposed of with relative ease, which is not the case with other acids commonly used for this purpose.

This new approach for measuring total oxalate allows the evaluation of the effect of process variables on the forms and partitioning of oxalate in mills, and the assessment of the effectiveness of various strategies to control oxalate scale deposition.

2.7   *Total oxalate*

2.7.1   *Process filtrates and effluents*

It is important to mix the samples well to establish and maintain, as closely as possible, the same equilibrium concentrations of dissolved and soluble forms of oxalate that existed under mill conditions at the time of sampling. Consequently, prior to sampling for oxalate analysis by IC, the samples were mixed thoroughly and warmed to the temperature prevailing at each sampling location. For the determination of total oxalate in process filtrates and effluents, refrigerated samples were first warmed to the temperature at which they were collected and mixed thoroughly for 5-10 minutes. An accurately

known volume (25 mL) or mass (25 g) of sample was then placed in a 50 mL Pyrex

beaker to which was added 0.60 mL MSA - the purpose of which is to dissolve all

insoluble forms of oxalate. The beaker was covered with Parafilm, placed on a magnetic

stirrer/hotplate and the contents were stirred vigorously with the aid of a Teflon-coated

stirring bar for 30 minutes at 60 °C. During the dissolution step, the MSA concentration

was ca. 2.5% v/v and the pH of the mixture was ≤ 1. After 30 minutes, the beaker and its

contents were removed from the hot plate, allowed to cool briefly, and quantitatively

transferred to a volumetric flask. If necessary, additional MSA was added to the flask

before dilution to volume so that the final concentration of MSA was approximately 0.5%

v/v. In most cases sample dilution was in the range of 1:20. An aliquot was taken from

the volumetric flask, filtered through a 0.45 μm membrane filter and delivered to an

autosampler tube for injection into the ion chromatograph. It is important to note that in

the case of total oxalate analysis, the MSA concentration in the diluted samples should be

maintained at or below 0.5% v/v. Therefore, if sample dilution is needed to bring the

peak area of oxalate within the linear range of the calibration plot, sufficient MSA must

be added during the dilution step so that 0.5% MSA is present once the final dilution has

been made.

2.7.2   *Pulp, pulp slurries, wood chips and scale deposits*

Into a 150 mL Pyrex beaker was added an accurately known mass of both sample (ca. 2

g) and water (ca. 100 g), 2.5 mL of MSA and a Teflon-coated stirring bar. The beaker

was covered with Parafilm, placed on a magnetic stirrer/hot plate and the contents were

vigorously mixed for 30 minutes at ca. 60 °C. Following the prescribed mixing period,

the sample was processed further (filtered and diluted) as described in section (i) above.

Portions of pulp slurries were centrifuged to enable separation of fibre-free supernatant.

2.8   Soluble oxalate

2.8.1   Process filtrates and effluents

Approximately 8 mL of warmed process filtrate or effluent was transferred to a 10 mL

polypropylene syringe, to which was attached, via luer lock fittings, a Millex-LCR 0.45

µm x 25 mm PTFE membrane filter (Millipore, Bedford, MA, USA). The contents of the

syringe were forced through the membrane filter and the last 5 mL of filtered sample was

collected in a small glass vial. Filtration through a 0.45 µm membrane was performed to

remove insoluble forms of oxalate present in the sample. An accurately known volume of

the filtered sample was transferred to a volumetric flask and diluted to volume with

water. A portion of the filtered, diluted sample was then transferred to an autosampler

tube for injection into the ion chromatograph.

2.8.2   Pulp, pulp slurries, wood chips and scale deposits

Pulp, pulp slurries, wood chips and scale deposits were first heated, mixed and/or ground

as described in section (iii), and then processed further as described in sections (ii) and

(iii), except that no MSA was added to the samples.

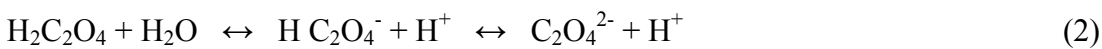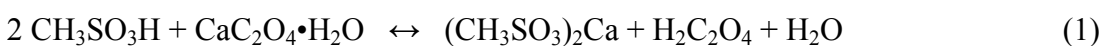## 3.   RESULTS AND DISCUSSION

3.1   *Analysis of soluble oxalate*

Ion chromatography (IC) coupled with conductivity detection is well suited for analyzing

soluble, low molecular weight inorganic and organic ions in aqueous solutions. Over the

years, several columns and eluent systems have been developed which afford good

separation of oxalic acid and/or oxalate anion in aqueous samples. The columns and

separation conditions chosen and used in this work are similar to those recommended by

Dionex for the analysis of common anions. The separation of standard solutions of

oxalate by itself and in combination with other anions prepared in water is shown in

Figure 1. As illustrated, the common anions found in pulp and paper mill samples are

well resolved and elute in less than 15 minutes.

3.2   *Dissolution of insoluble oxalate*

One of the major requirements for the analysis of total oxalate was to find a reliable

method for dissolving the insoluble forms of oxalate. It has been reported that MSA can

dissolve oxalate at room temperature. The effectiveness of MSA when compared to

inorganic, non oxidizing acids such as HCl, is that MSA forms a stable, water-soluble

complex with several metals, including calcium [31,32] to yield calcium

methanesulphonate, $(CH_3SO_3)_2Ca)$ as illustrated by its reaction with COM in reaction 1,

whereas HCl reacts more slowly with COM to form oxalic acid and calcium chloride.

The oxalic acid formed from reaction 1 may ionize to different extents, depending upon

the pH, and exist in one or more forms (all of which are soluble) as shown in reaction 2.

$$2\ CH_3SO_3H + CaC_2O_4 \cdot H_2O\ \leftrightarrow\ (CH_3SO_3)_2Ca + H_2C_2O_4 + H_2O \tag{1}$$

$$H_2C_2O_4 + H_2O\ \leftrightarrow\ H\ C_2O_4^- + H^+\ \leftrightarrow\ C_2O_4^{2-} + H^+ \tag{2}$$

3.3   *Application of MSA in IC analysis of total oxalate*

Repeated injections of aqueous MSA solutions ranging in concentration from 0.1 to 5%

(v/v) were made to test the compatibility of MSA with the IC column. The results showed

that the retention time, peak area and peak shape of oxalate standards prepared in water

and aqueous MSA were essentially identical, thus implying that MSA was fully

compatible and did not degrade the IC column or suppression system. A single peak

attributable to methanesulphonate ($CH_3SO_3^-$ or MS^-) eluted in or near the water dip and

thus was not retained by the column. In addition, a small peak eluted at the same

retention time as sulphate, which is probably a minor artifact from manufacture of the

MSA [31]. However, as shown in Figure 2, the elution of the oxalate ion is not affected by

the presence of MSA or any other anions present in the sample. Calibrations curves for

the analysis of oxalate in the presence of 0.5% v/v MSA showed that the presence of

0.5% or less MSA in the standards did not significantly affect the response of the

conductivity detector to oxalate and a strong linear relationship was found over the

concentration range studied (Figure 3).

Conditions necessary to effect complete dissolution of aqueous suspensions of calcium

oxalate with MSA, we studied by varying the concentration of calcium oxalate and the

mixing time under constant MSA and temperature conditions. The calcium oxalate

suspensions were prepared by combining equal volumes of equimolar solutions of

calcium chloride and sodium oxalate in a constant final volume of water. The resultant

aqueous suspensions of calcium oxalate were then mixed vigorously on a hot plate for

five minutes at 60 °C, and then a known volume of MSA was added and the suspensions

were mixed for an additional 0, 5, 10, 20 and 30 minutes. Samples of the suspensions

were taken at each interval, filtered through 0.45 μm PTFE membrane filters and the

filtrates were diluted and analyzed to determine the concentration of oxalate present. As

summarized in Table 1, high concentrations of calcium oxalate, well beyond the levels

expected to be present in most pulp and paper mill process samples, were dissolved

within 5 minutes. These findings suggest that MSA will dissolve COM in any type of

pulp and paper sample.

3.4 Analysis of kraft mill samples

Vat samples from the last brownstock (BStock), the D_0 and Eo_P, D_1 and D_2 washers were

collected from three kraft mills and analyzed for soluble and insoluble oxalate content.

As shown in Table 2 for mills A and B samples, the concentration of soluble and

insoluble oxalate varied considerable between mills A and B and between the various

stages. For example, the brownstock sample in Mill A contained nearly 2.5 times more

soluble oxalate than the same stage in mill B. However, the percentage of insoluble

oxalate was much lower in mill A brownstock than in the corresponding mill B sample.

The oxalate present in the brownstock samples originates from the wood supply and that

which is formed by the degradation of lignin and carbohydrates during pulping. Both D_0

vat samples contained less oxalate that the corresponding brownstock samples, and both

samples contained a high percentage of insoluble oxalate, which in the case of the mill B

sample, exceeded the level of soluble oxalate. The highest levels of oxalate were found in

the E_{OP} vat samples, which contained 3-5 times more soluble oxalate than D_0 vat

samples. The E_{OP} vat samples also contained the least insoluble oxalate.

Selected samples were spiked with soluble and insoluble forms of oxalate to determine

the accuracy of our method. As also shown in Table 2, the recoveries for both forms of

oxalate ranged from 95-105%, which indicates that the method is suitable for quantitative

analysis in both acidic and alkaline process samples. Figure 4 shows the separation of

soluble oxalate from other anions in D_0 and E_{OP} vat samples from mill A. Figure 5 shows

the separation of total oxalate from other anions in a D_0 sample from mill A. In both

separations, it is clear that oxalate is well resolved from other anions and free from

interferences in both types of samples.

3.5   *Comparison of methods for the analysis of total oxalate*

To our knowledge, the only other published IC method for determining oxalate in pulp

and paper samples is that of Reimann et al. [29]. Their method was developed for and

applied only to kraft bleach filtrates, and measures total oxalate by mixing aqueous

samples in the presence of a strong cation-exchange resin to dissolve insoluble forms of

oxalate, followed by IC analysis of the dissolved oxalic acid. As a further test of our

method, we analyzed several filtrate samples from a third kraft mill by our method and

that of Reimann et al. As indicated in Table 3, we found excellent agreement between the

two methods for the five different filtrate samples. In the course of this work we

discovered that the cation-exchange resin recommended and purchased from Aldrich

contained a red, water soluble dye (probably formed during the resin manufacturing

process), that if injected into the IC, can adsorb to and damage the IC columns. However,

we found that we could remove the dye quite effectively by simply washing the resin

with 50 mL of 1 M HCl and then with copious amounts of Milli-Q water until the pH of

eluate from the resin was neutral. This simple procedure not only removes any dye that is

present, but also ensures that the resin is fully protonated prior to use. The advantage of

our method over that of Reimann et al., is that it is simpler to perform and steps such as

resin washing to remove the dye, which can harm expensive IC columns, and filtration of

resin containing samples prior to IC analysis are not necessary in our approach. In

addition, our method has been validated for a broader range of samples, including paper,

pulp, and scale deposits.

4.   CONCLUSIONS

A new and rapid method has been developed for measuring soluble and insoluble forms

of oxalate in kraft pulp and paper matrices. Spike-recovery experiments showed that both

forms of oxalate are quantitatively determined. The method can also be applied to the

analysis of calcium oxalate in scale deposits.

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Table 1. Effect of mixing time and aqueous MSA concentration on the dissolution of aqueous calcium oxalate suspensions. All experiments were conducted at 60 °C. See experimental section and text for additional details.

Experiment No.	Mixing Time (min)	$[CaC_2O_4]$ (mM)	$[CaC_2O_4]$ (mg/L)	[MSA] (%, v/v)	CaC_2O_4 Dissolved (%)
1	0	1.15	147	0	8
2	5	1.15	147	2.5	98
3	10	1.15	147	2.5	97
4	20	1.15	147	2.5	98
5	30	1.15	147	2.5	99
6	0	1.70	218	0	8
7	5	1.70	218	2.5	97
8	10	1.70	218	2.5	98
9	20	1.70	218	2.5	98
10	30	1.70	218	2.5	100

Table 2. Soluble and insoluble levels in, and recovery of added soluble and insoluble oxalate for kraft mill brownstock (BStock), D_0 and Eop pulp slurries from Mills A and B. Soluble oxalate added in the form of aqueous sodium oxalate. Insoluble oxalate added in the form of solid COM.

Sample	$[C_2O_4^{2-}]$, mg/kg oven dry pulp					Recovery
	Soluble	Insoluble	Added		Found	%
			Soluble	Insoluble		
Mill A						
BStock	4530	-	4000	-	3890	97
D_0	2130	-	2000	-	1950	98
Eop	12800	-	6000	-	5900	98
BStock	-	880	-	1000	1050	105
D_0	-	1560	-	1500	1480	99
Eop	-	600	-	500	520	104
Mill B						
BStock	1865	-	2000	-	1920	96
D_0	1650	-	1500	-	1580	105
Eop	8950	-	4000	-	4100	103
BStock	-	1580	-	1500	1450	97
D_0	-	2195	-	2000	2060	103
Eop	-	345	-	500	515	103

Table 3. Comparison of total oxalate results obtained by the current method and that of Reimann et al. [27], for kraft process filtrates from Mill C.

Sample	Total Oxalate Concentration, mg/L	
	Current Work	Reimann et al.
BStock	30	29
D_0	61	60
Eop	133	125
D_1	16	14
D_2	10	10

FIGURE CAPTIONS

Figure 1. Separation of oxalate in a standard solution by itself (upper trace) and in a standard mixture with five additional anions, including chloride, nitrite, phosphate, chlorate, sulphate (lower trace). Both solutions were prepared in water and contained 2.5 mg/L of oxalate. See experimental section for other conditions.

Figure 2. Separation of oxalate in standard solutions prepared in 0.5% v/v MSA in water (upper trace) and in water (lower trace). Oxalate was present at 2.5 mg/L in each solution. See experimental section for other conditions.

Figure 3. Calibration plot showing the linear relationship between peak area and the concentration of oxalate in standard solutions prepared in water (open, inverted triangles) and in 0.5% v/v MSA in water (black, filled circles). See experimental section and Section 2.4 for further details.

Figure 4. Separation of soluble oxalate in samples of kraft D_0 (upper trace), Eop (middle trace) filtrates and in a standard solution containing several common anions, including 2.5 mg/L oxalate (bottom trace). The samples and the standard were prepared in water. See experimental section for other conditions.

Figure 5. Separation of total oxalate in a sample of kraft D_0 filtrate (upper trace) and in a standard solution containing several common anions, including 2.5 mg/L oxalate (bottom trace). The sample and standard were prepared in 0.5% v/v MSA in water. See experimental section for other conditions.
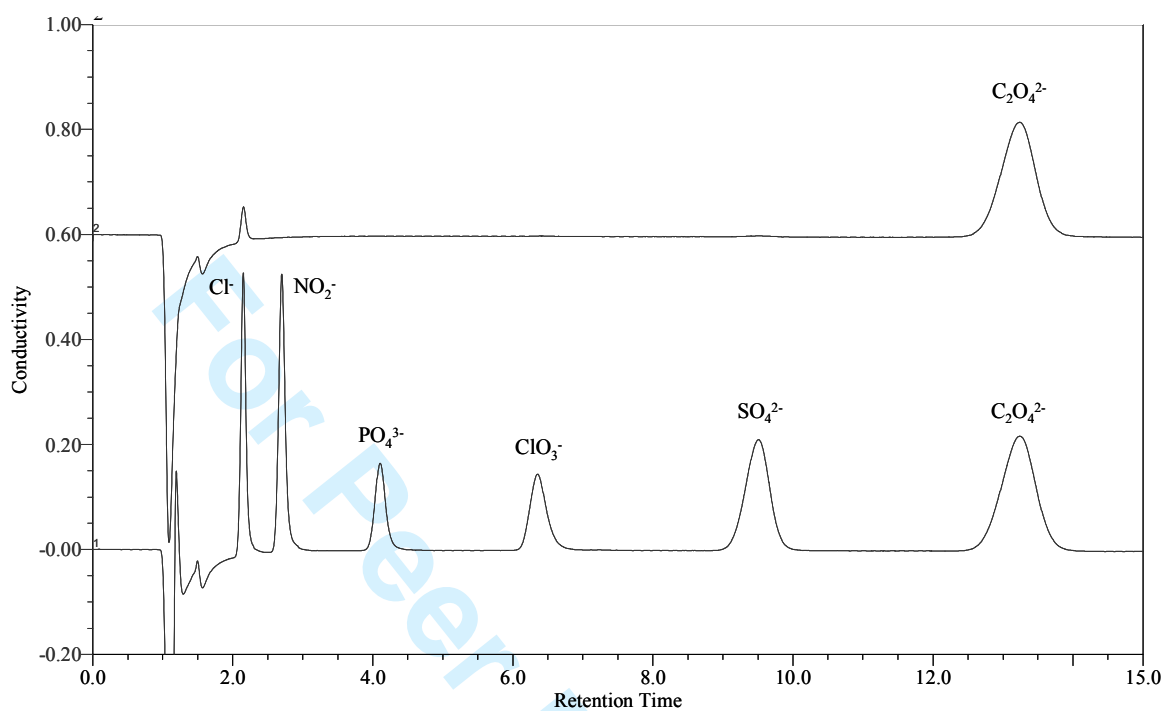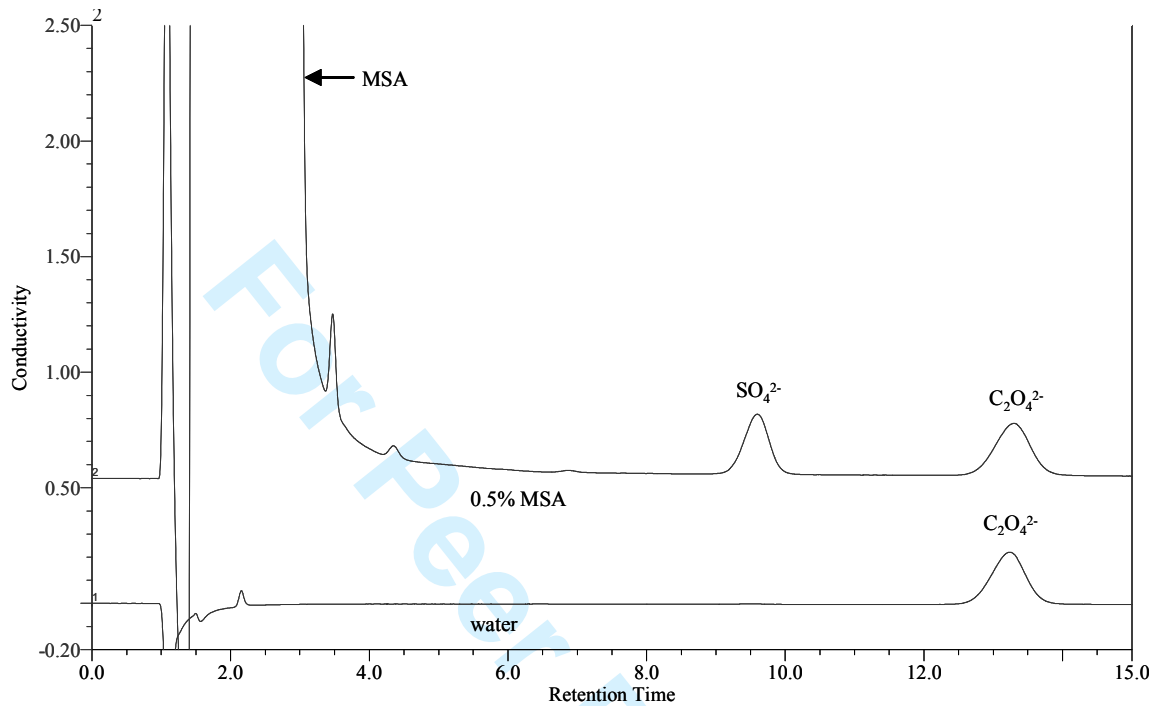
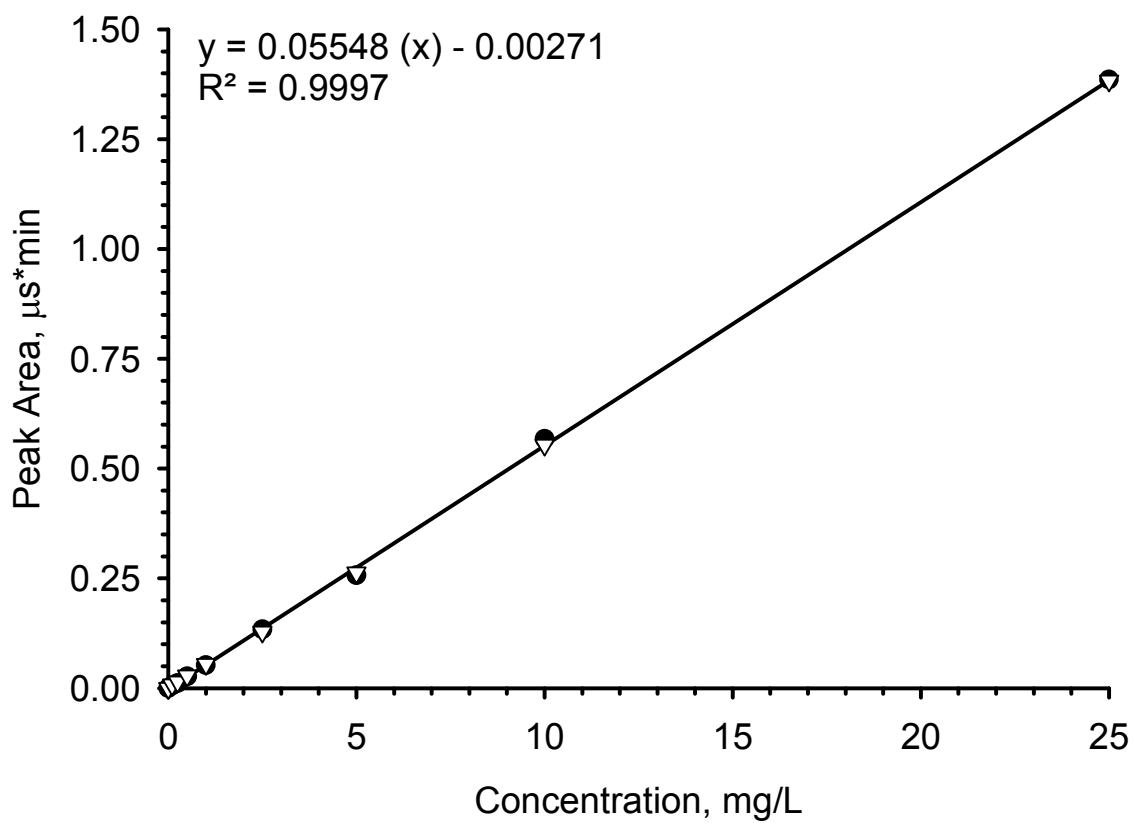Figure 1.

Figure 2.

Figure 3

y = 0.05548 (x) - 0.00271
R^2 = 0.9997

Peak Area, μs*min (y-axis, 0.00 to 1.50)

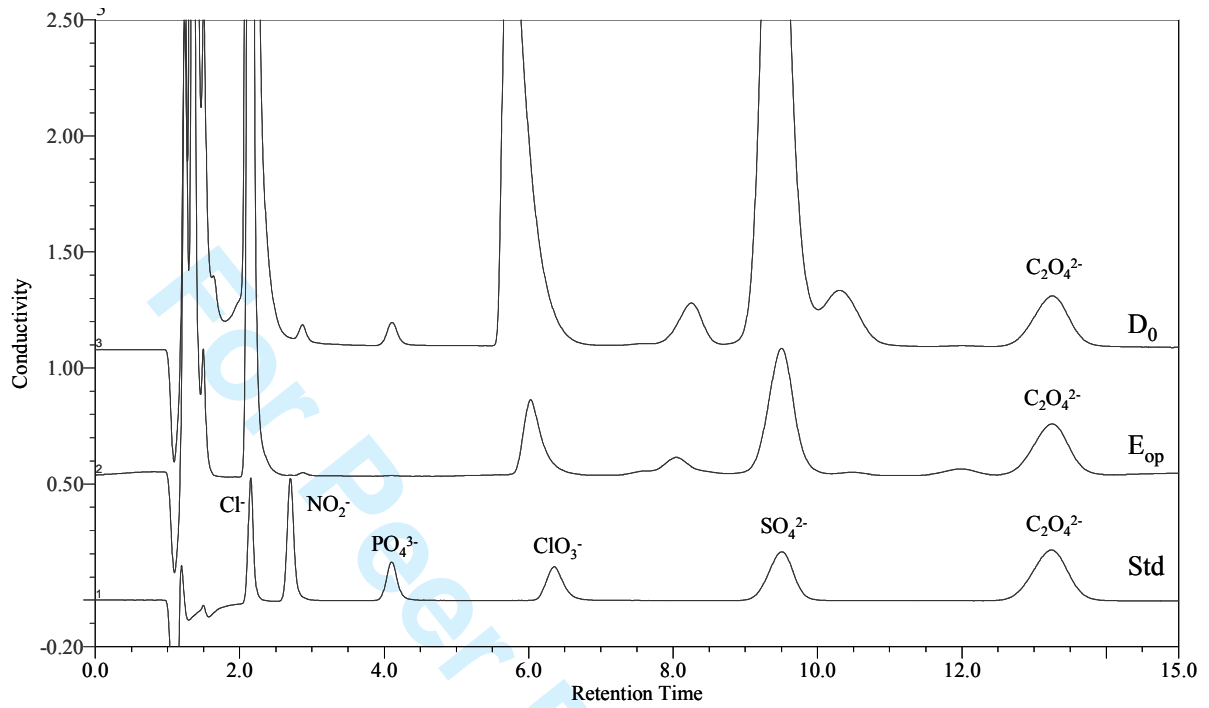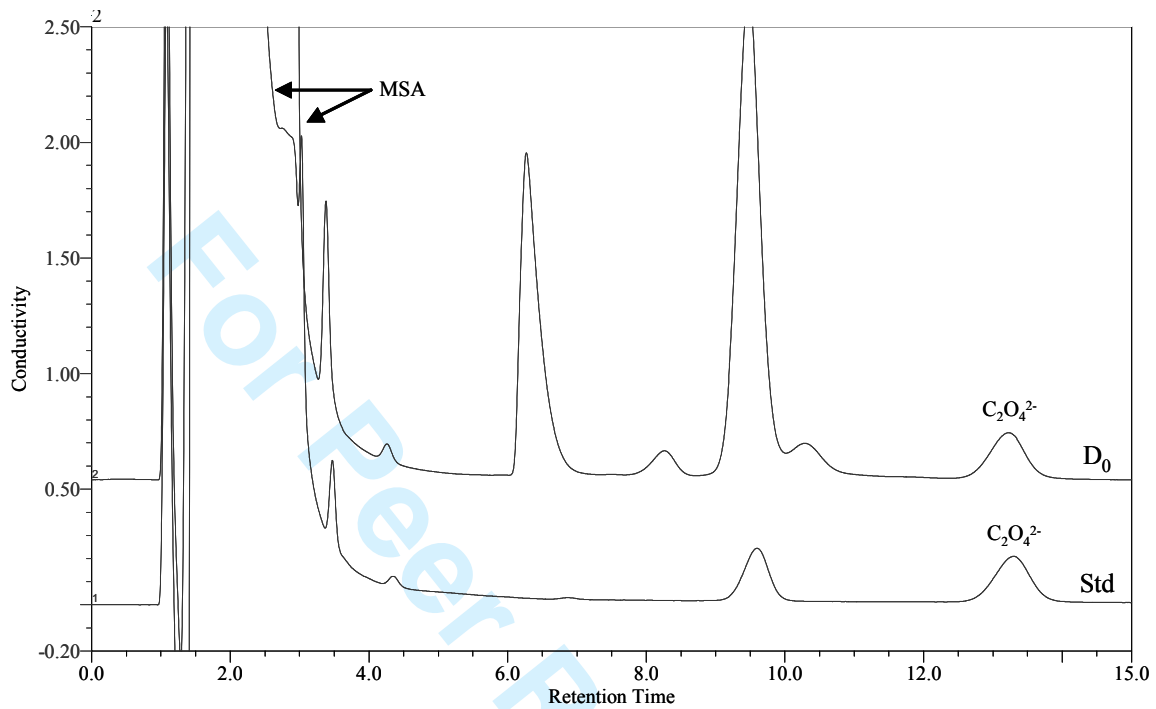Concentration, mg/L (x-axis, 0 to 25)

Figure 4

Figure 5

FIGURE CAPTIONS

Figure 1. Separation of oxalate in a standard solution by itself (upper trace) and in a standard mixture with five additional anions, including chloride, nitrite, phosphate, chlorate, sulphate (lower trace). Both solutions were prepared in water and contained 2.5 mg/L of oxalate. See experimental section for other conditions.

Figure 2. Separation of oxalate in standard solutions prepared in 0.5% v/v MSA in water (upper trace) and in water (lower trace). Oxalate was present at 2.5 mg/L in each solution. See experimental section for other conditions.

Figure 3. Calibration plot showing the linear relationship between peak area and the concentration of oxalate in standard solutions prepared in water (open, inverted triangles) and in 0.5% v/v MSA in water (black, filled circles). See experimental section and Section 2.4 for further details.

Figure 4. Separation of soluble oxalate in samples of kraft D_0 (upper trace), Eop (middle trace) filtrates and in a standard solution containing several common anions, including 2.5 mg/L oxalate (bottom trace). The samples and the standard were prepared in water. See experimental section for other conditions.

Figure 5. Separation of total oxalate in a sample of kraft D_0 filtrate (upper trace) and in a standard solution containing several common anions, including 2.5 mg/L oxalate (bottom trace). The sample and standard were prepared in 0.5% v/v MSA in water. See experimental section for other conditions.
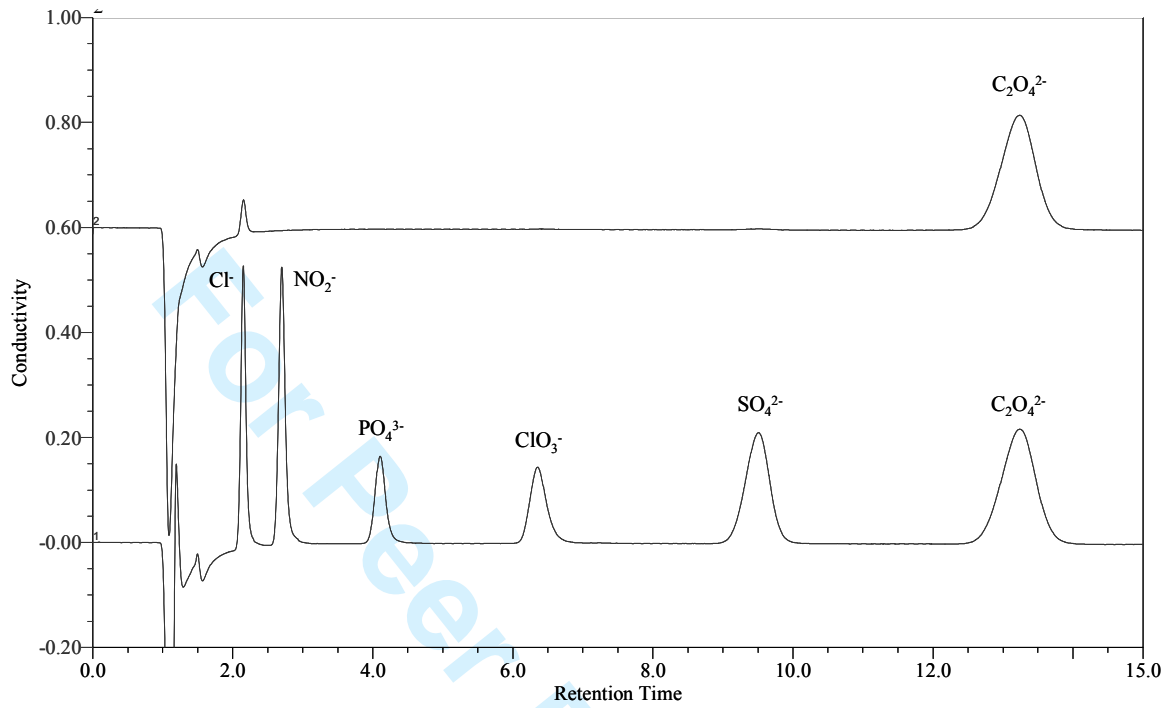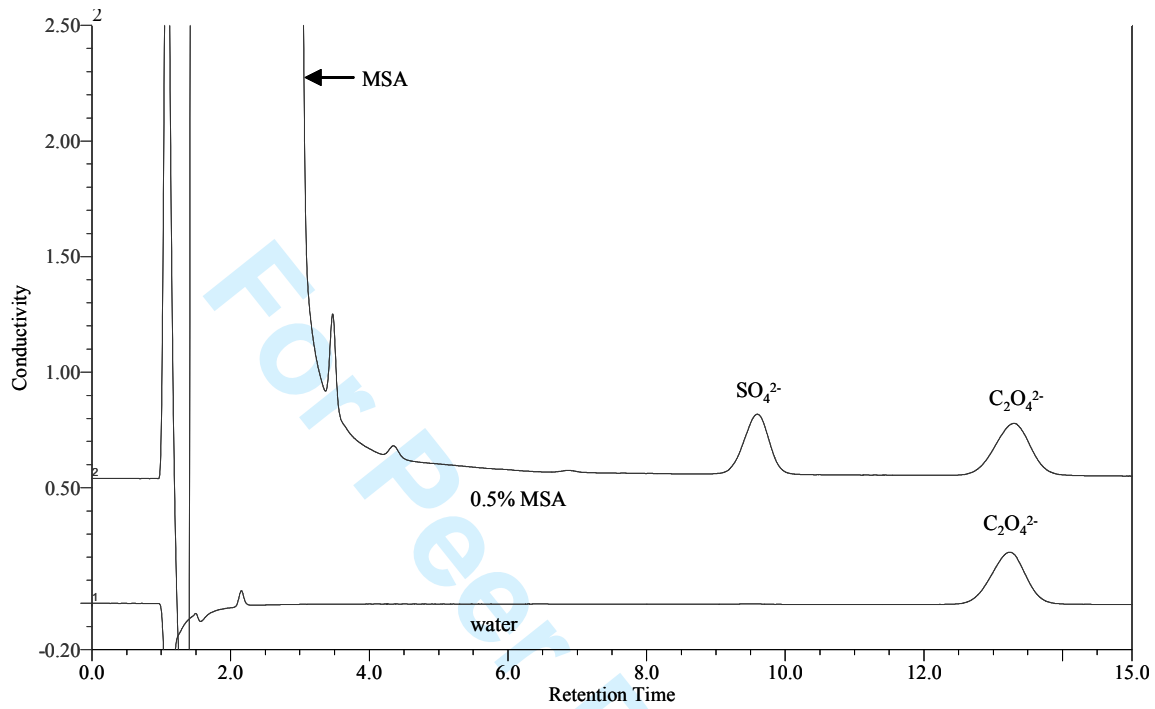
Figure 1.

Figure 2.

Figure 3

$y = 0.05548 (x) - 0.00271$
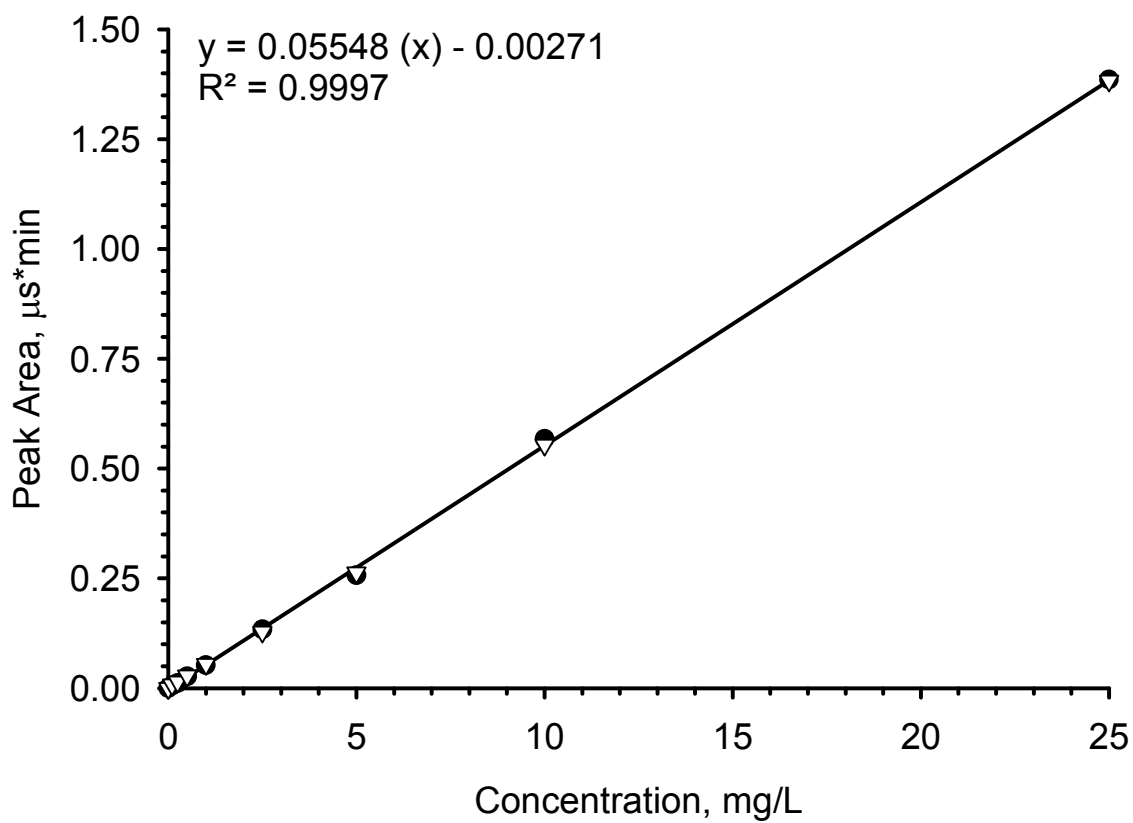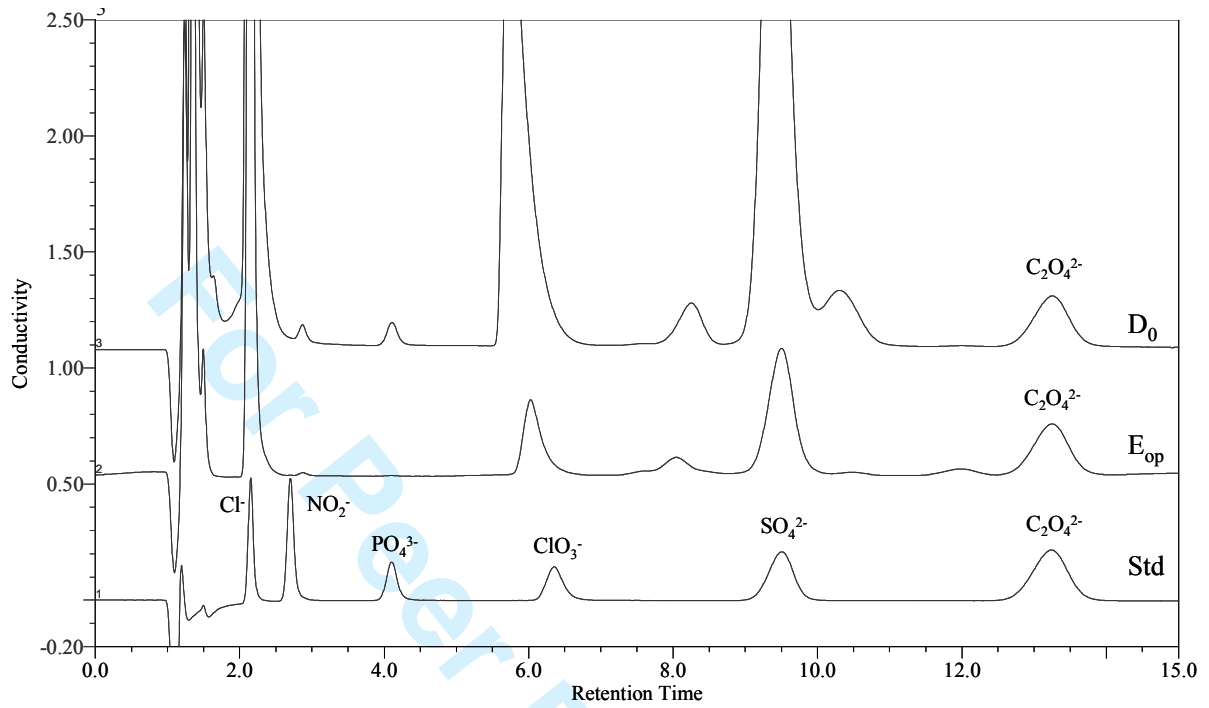$R^2 = 0.9997$

Peak Area, μs*min

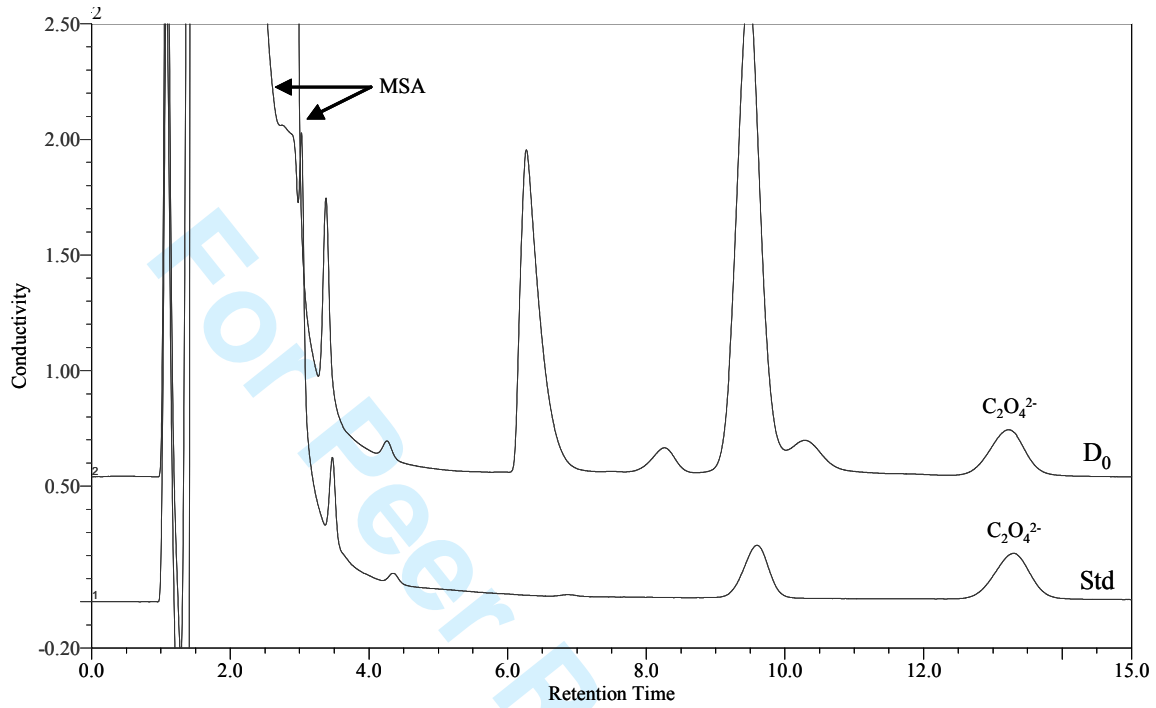Concentration, mg/L

Figure 4

Figure 5

Table 1. Effect of mixing time and aqueous MSA concentration on the dissolution of aqueous calcium oxalate suspensions. All experiments were conducted at 60 °C. See experimental section and text for additional details.

Experiment No.	Mixing Time (min)	$[CaC_2O_4]$		[MSA] (%, v/v)	CaC_2O_4 Dissolved (%)
		(mM)	(mg/L)		
1	0	1.15	147	0	8
2	5	1.15	147	2.5	98
3	10	1.15	147	2.5	97
4	20	1.15	147	2.5	98
5	30	1.15	147	2.5	99
6	0	1.70	218	0	8
7	5	1.70	218	2.5	97
8	10	1.70	218	2.5	98
9	20	1.70	218	2.5	98
10	30	1.70	218	2.5	100

Table 2. Soluble and insoluble levels in, and recovery of added soluble and insoluble oxalate for kraft mill brownstock (BStock), D_0 and Eop pulp slurries from Mills A and B. Soluble oxalate added in the form of aqueous sodium oxalate. Insoluble oxalate added in the form of solid COM.

Sample	$[C_2O_4^{2-}]$, mg/kg oven dry pulp					Recovery
	Soluble	Insoluble	Added		Found	%
			Soluble	Insoluble		
Mill A						
BStock	4530	-	4000	-	3890	97
D_0	2130	-	2000	-	1950	98
Eop	12800	-	6000	-	5900	98
BStock	-	880	-	1000	1050	105
D_0	-	1560	-	1500	1480	99
Eop	-	600	-	500	520	104
Mill B						
BStock	1865	-	2000	-	1920	96
D_0	1650	-	1500	-	1580	105
Eop	8950	-	4000	-	4100	103
BStock	-	1580	-	1500	1450	97
D_0	-	2195	-	2000	2060	103
Eop	-	345	-	500	515	103

Table 3. Comparison of total oxalate results obtained by the current method and that of Reimann et al. [27], for kraft process filtrates from Mill C.

Sample	Total Oxalate Concentration, mg/L	
	Current Work	Reimann et al.
BStock	30	29
D_0	61	60
Eop	133	125
D_1	16	14
D_2	10	10