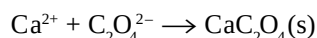


Oxalic acid formation during ECF and TCF bleaching of kraft pulp

ANNA ELSANDER, MONICA EK, AND GÖRAN GELLERSTEDT

THE TERM “ENVIRONMENTAL considerations,” in its narrowest sense, involves compliance with governmental regulations. However, public concern for the environment has moved this issue into the broader arenas of marketing and corporate credibility. Consequently, many pulp mills are working toward closure, aiming to reduce both pollution and fresh water consumption. The principal challenge is learning how to deal with the subsequent buildup of organic and inorganic materials in the process streams.

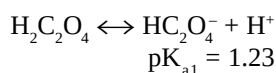
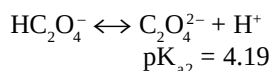
Oxalic acid is one of the organic substances formed in pulping and bleaching of chemical pulp. Together with calcium ions, which are abundant in the systems, oxalic acid forms the insoluble salt calcium oxalate according to the following reaction:



Calcium oxalate can form porcelainlike deposits on the equipment of the bleach plant, for example in filtrate tanks and on washing filter wires. This kind of scaling problem can limit the degree of closure in a mill that is practically feasible.

While oxalic acid is formed during pulping and bleaching, it is also present in native wood, which typically contains about 0.1–0.4 kg oxalic acid/metric ton (1) for both softwood and hardwood species. The green parts of the tree contain ten times more oxalic acid than the woody part (2).

Oxalic acid is a dicarboxylic acid, with the following pK_a values at 25°C:



The second pK_a value increases with increasing temperature, which means that a higher pH value is required for precipitation of calcium oxalate to occur. The solubility product of the precipitate also increases at higher temperatures. The solubility product of calcium oxalate in water is $2 \times 10^{-9} \text{ M}^2$, but in process streams it is higher. The higher solubility in process streams is a function of the high temperatures as well as the high concentrations of dissolved organic material, which can act as a complexing agent and thereby bind calcium ions (2). The presence of EDTA (ethylenediamine tetraacetic acid) and DTPA (diethylenetriamine pentaacetic acid) in the filtrates also increases the solubility of calcium oxalate in the same way. Nevertheless, this enhanced solubility will not be enough to avoid precipitation when the concentrations of calcium and oxalate ions are increased. The risk of forming calcium oxalate deposits is greatest when the pH is between 4 and 8. Below pH 4, the oxalate ions become protonated (as seen in the given equations), while above pH 8, the carbonate ions in the system outvalue the oxalate ions in the competition for calcium ions.

ABSTRACT

Formation of oxalic acid during bleaching of softwood kraft pulp was studied. The bleaching agents used were oxygen, hydrogen peroxide, chlorine dioxide, peracetic acid, and ozone. Formation of oxalic acid increased linearly with the reduction in kappa number. However, bleaching with peracetic acid produced less oxalic acid than the other bleaching agents. In ozone bleaching, about one-third of the oxalic acid formed is adsorbed on the pulp and not released until pulp pH is increased during a later stage, where it could combine with calcium ions to produce a calcium oxalate scale.

Application:

Mills that are increasing closure in the bleach plant can avoid scaling problems by tailoring their operations to minimize formation of oxalic acid.

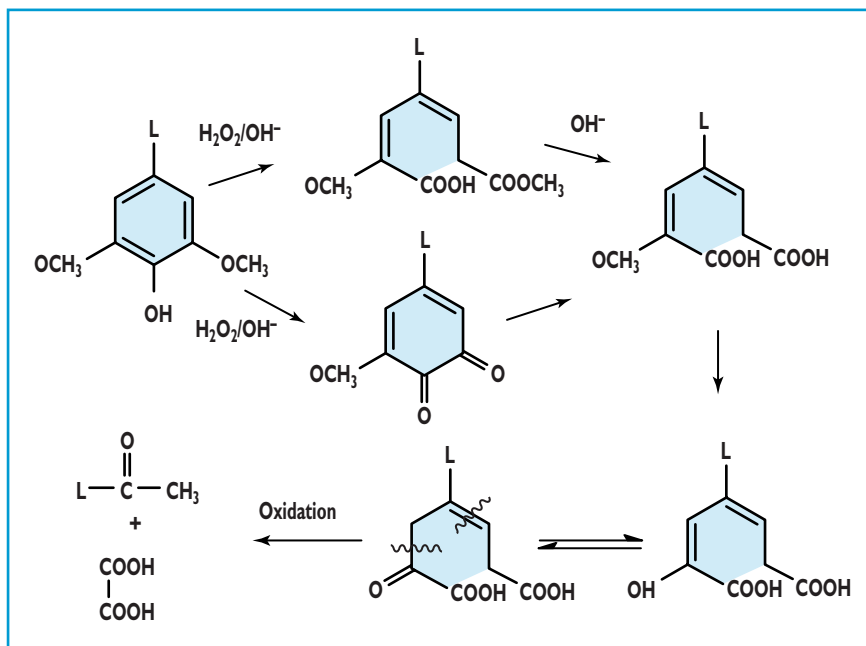
This leads to the formation of calcium carbonate, which can also form troublesome deposits (3).

Precipitation of calcium oxalate is often initiated by changes in temperature or pH. This can happen, for example, when alkaline P-stage filtrates, rich in oxalate, are mixed with acidic filtrates having high calcium levels.

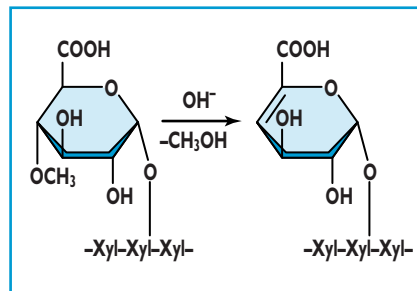
This research focuses on the formation of oxalic acid in the presence of a variety of bleaching chemicals that are commonly applied during bleaching of softwood kraft pulp. The formation of oxalic acid in a conventional elemental-chlorine free (ECF) bleach sequence and in three modern bleach sequences was also studied.

ORIGIN OF OXALIC ACID

Most of the oxalic acid found in the pulp is formed by oxidative reactions in the bleach plant. Until recently, lignin was thought to be the



1. Reaction between hydrogen peroxide and lignin (5)



2. Formation of hexenuronic acid during pulping

more oxalic acid was formed from lignin than xylan in all cases. This indicates that lignin is the major source of oxalic acid during bleaching of kraft pulp.

EXPERIMENTAL

The influence of different bleaching agents and bleaching sequences on the formation of oxalic acid was studied. The pulp used was a commercially produced oxygen-delignified softwood kraft pulp of kappa no. 14.6. The formation of oxalic acid in a traditional ECF sequence was also studied, but in this case, the pulp was an unbleached softwood kraft pulp (kappa no. 26) that was oxygen delignified in the laboratory.

With each bleaching agent, the bleaching time or the charge was varied, depending on the reaction rate. Before the acidic bleaching stages, the pulp was washed with a mild acidic wash (pH 2) to remove calcium in order to prevent calcium oxalate from precipitating during the experiments. Prior to hydrogen peroxide bleaching, the pulp was treated with EDTA.

All nonpressurized bleaching experiments were performed in polyethylene bags where the pulp was diluted with deionized water to 10% consistency. After the charge of bleaching chemicals and pH adjustment, the sealed bags were kneaded in a special device and placed in a thermostatic water bath for the time desired. Table I provides more detailed information about the conditions used for the various bleaching agents and the different bleaching sequences.

	FIRST STAGE (OP)	SECOND STAGE (D) (Paa)* (Z)		THIRD STAGE (P)	FOURTH STAGE (PO)
Concentration, %	12	10	10	10	12
Temperature, °C	100	70	70	45	70
Time, min	5-120	60	60	5	15-360
Charge, kg/metric ton	5	4-18	10-40	2.5-6.5	40
End pH	11.0	3.5	5.5	2.5	11.0
Pressure, bar	7	...	...	5	...

* Peracetic acid

1. Conditions used in the bleaching experiments

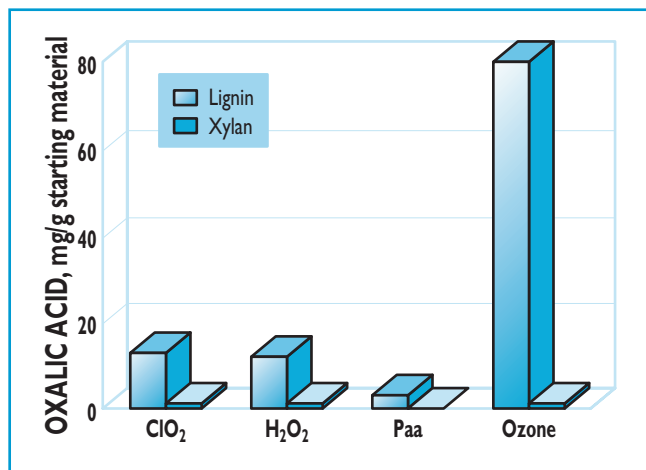
only source of oxalic acid (1). Experiments involving formation of oxalic acid from different lignin models are reported by Kratzl *et al.* (oxygen/alkali treatment of bicresol) (4) and Yamamoto *et al.* (ozonation of catechol) (5).

When lignin is attacked by alkaline hydrogen peroxide, the radical species present in the bleaching system attack the aromatic ring to form muconic acid. This was studied by Kempf and Dence (6), who reported oxalic acid to be one of the end products, as seen in Fig. 1.

More recently, it has been reported that xylan can also give rise to oxalic acid (7). Under the alkaline conditions in pulping, the 4-*o*-Me-glu-

cronic acid substituents attached to the xylan backbone are converted into hexenuronic acid groups (8, 9). As seen in Fig. 2, the unsaturated structure is formed by eliminating methanol from the glucuronic acid. In the bleach plant, the double bond of the hexenuronic acid is susceptible to attack from electrophilic bleaching agents such as ozone. One of the reaction products formed is oxalic acid.

In a comparative study (10), kraft lignin from black liquor and alkali-treated xylan were oxidized with different bleaching agents. The hexenuronic acid content in the modified xylan was measured using a new method (11). As seen in Fig. 3,



3. Formation of oxalic acid during oxidation of xylan and lignin with different bleaching agents

The ECF sequence studied was a D(E+P)D(E+P)D sequence. The initial pulp kappa number (after oxygen delignification in the laboratory) was 13.7. The total charge of chlorine dioxide in the sequence was 17 kg/metric ton, and the hydrogen peroxide charge was 6 kg/metric ton. The other conditions in this sequence were chosen to achieve full brightness and good pulp quality.

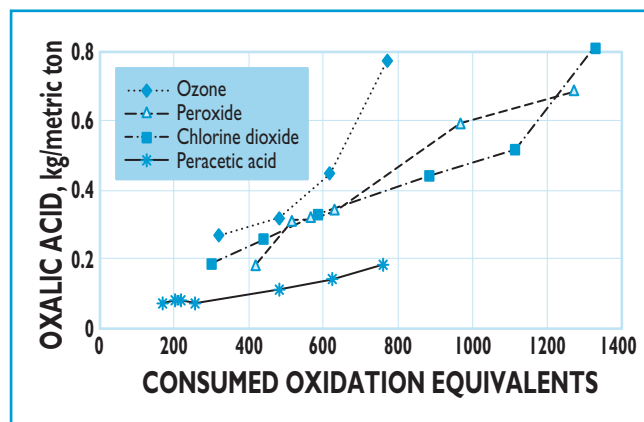
Three modern bleach sequences also were studied on the oxygen-delignified pulp: (OP)DQ(PO), (OP)PaaQ(PO), and (OP)ZQ(PO).

The oxalic acid in the filtrates from the different bleaching stages and in some pulps was analyzed by ion chromatography (12). Kappa number was determined in accordance with SCAN C 1:77.

RESULTS AND DISCUSSION

Bleaching agents

All bleaching agents promote formation of oxalic acid as the delignification proceeds. This is shown in Fig. 4, where formation of oxalic acid is plotted against consumed oxidation equivalents with each of four bleaching



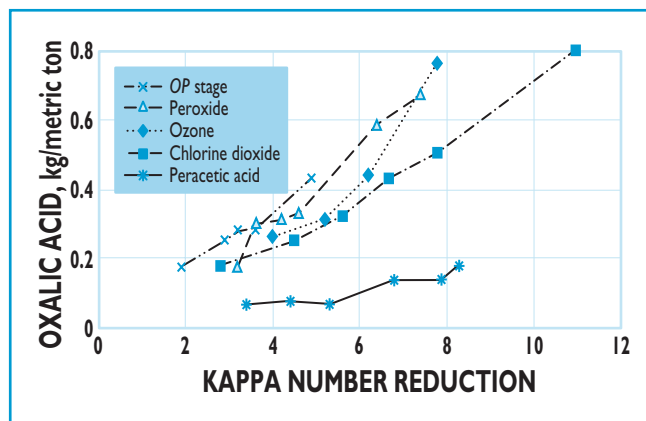
4. Oxalic acid formed vs. consumed oxidation equivalents with different bleaching agents

agents. Peracetic acid (Paa) formed less oxalic acid compared with the other bleaching agents. This distinctive behavior of peracetic acid is easier to see when the formation of oxalic acid is plotted against the kappa number reduction for each bleaching agent, as seen in Fig. 5. Hydrogen peroxide, chlorine dioxide, and ozone bleaching gave rise to approximately 80 g oxalic acid/metric ton per delignified kappa number unit, while peracetic acid bleaching results in about 20 g/metric ton per kappa number unit.

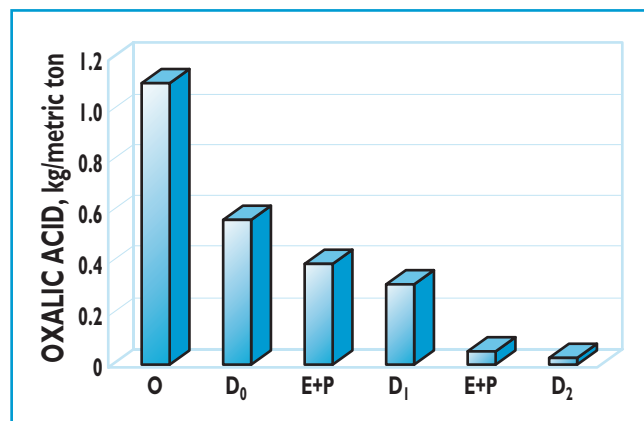
Kappa number analysis is not the best way of measuring delignification, since the hexenuronic groups also contribute to the kappa number. However, kappa number is widely used to evaluate bleaching sequences, so it was also used as the benchmark in this work.

Conventional ECF bleaching sequence

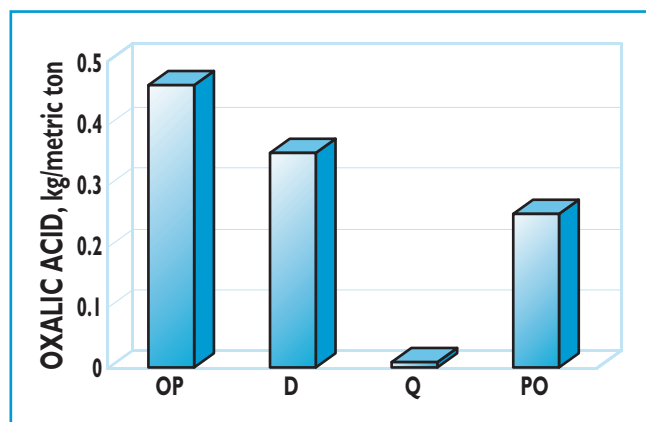
Figure 6 shows the formation of oxalic acid in each stage along a conventional ECF bleaching sequence, OD(E+P)D(E+P)D. The pulp used was an unbleached softwood pulp. The largest amount of oxalic acid was formed during the oxygen delignification. This seldom leads to scaling problems because the pH is too high for



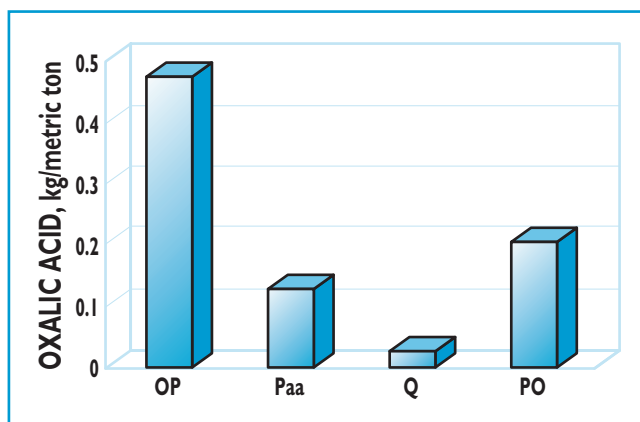
5. Oxalic acid formed vs. kappa number reduction with different bleaching agents



6. Oxalic acid formed in each stage of a conventional ECF sequence



7. Oxalic acid formed in each stage of an (OP)DQ(PO) sequence



8. Oxalic acid formed in each stage of an (OP)PaaQ(PO) sequence

	FIRST STAGE (OP)		SECOND STAGE (D), (Paa), or (Z)		THIRD STAGE (Q)		FOURTH STAGE (PO)	
	Oxalic acid	Kappa number	Oxalic acid	Kappa number	Oxalic acid	Kappa number	Oxalic acid	Kappa number
(OP)DQ(PO)	0.48	10	0.36	2.9	0.01	2.8	0.26	1.6
(OP)PaaQ(PO)	0.48	10	0.13	6.1	0.03	5.5	0.21	3.6
(OP)ZQ(PO)	0.48	10	0.45	5.9	0.36	4.2	0.22	2.6

II. Oxalic acid (kg/metric ton) formed during each stage of the three bleaching sequences and kappa number after each stage

calcium oxalate to form. However, depending on the efficiency of the wash after oxygen delignification, oxalic acid can be transferred with the pulp into the bleach plant.

Modern bleaching sequences

Three alternative bleaching sequences—(OP)DQ(PO), (OP)PaaQ(PO), and (OP)ZQ(PO)—also were studied. Oxygen-delignified pulp was used in these bleaching experiments. All three sequences included a second oxygen stage and a pressurized peroxide stage. The sequences were performed with one of three bleaching agents—chlorine dioxide, peracetic acid, or ozone—applied after the second oxygen stage.

Formation of oxalic acid in the chlorine dioxide-based sequence can be seen in **Fig. 7**. A similar sequence, but based on peracetic acid instead of chlorine dioxide, is shown in **Fig. 8**. The amount of oxalic acid formed in the peracetic acid stage was low, as expected. Another interesting point is that the formation of

oxalic acid in the pressurized peroxide stage is slightly lower in this sequence than in the former, despite the higher kappa number in the same position. The total delignification in this sequence was less than in the corresponding D sequence, as seen in **Table II**.

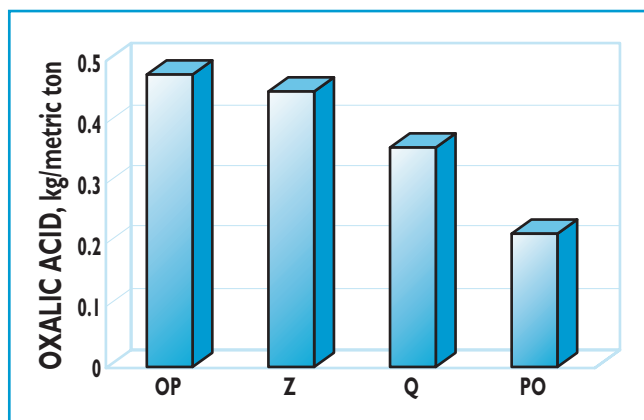
The last sequence was carried out with an ozone bleaching stage in the second position. The results in **Fig. 9** show that the ozone stage gave rise to more oxalic acid than did the chlorine dioxide and peracetic acid stages in the same position. The most remarkable thing about this sequence, however, is the high amount of oxalic acid liberated in the Q stage. In this stage, no oxalic acid is formed, and the pulp was thoroughly washed after the ozone stage to avoid carryover. Yet 0.3 kg of oxalic acid per metric ton was adsorbed by the pulp and released in the following Q stage when the pH was raised. This adsorption was not caused by precipitation of calcium oxalate, since calcium was removed

from the pulp prior to the ozone bleaching. One possible explanation could be that oxalic acid at this pH (about pH 2) partly exists as diprotonated. This undissociated oxalic acid has a low solubility in water and could therefore “precipitate” on the fibers. Another explanation could be the presence of oxidized groups in lignin or carbohydrates in the pulp. Such groups could release oxalic acid as the pH is raised in a later stage. However, this phenomenon of oxalic acid adsorption in pulp was not observed in chlorine dioxide bleaching, despite a similar pH during bleaching.

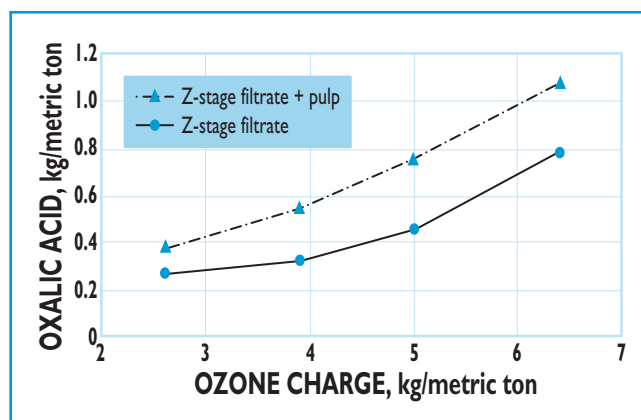
The kappa numbers and the oxalic acid formed in each stage of the three bleaching sequences are listed in **Table II**. The pulp used was an oxygen-delignified softwood pulp of kappa no. 14.6.

Ozone bleaching

A closer look at the formation of oxalic acid during ozone bleaching confirms the phenomenon proposed to explain the elevated level in the Q stage. The lower line in **Fig. 10** represents the oxalic acid found in the filtrate, while the upper line represents the oxalic acid found in the filtrate plus the oxalic acid found in the washed pulp. About 30% of the oxalic acid formed during ozone bleaching was adsorbed on the pulp and not released until the following Q stage. No adsorbed oxalic acid was found in chlorine dioxide-bleached pulp. According to these



9. Oxalic acid formed in each stage of an (OP)ZQ(PO) sequence



10. Oxalic acid formed at different ozone charges during ozone bleaching

results, ozone is the bleaching agent that forms the most oxalic acid.

CONCLUSION

Formation of oxalic acid during bleaching increases linearly with the reduction in kappa number. This was true for all bleaching agents studied. However, peracetic acid showed significantly lower formation than the other bleaching agents. Ozone bleaching showed the greatest formation of oxalic acid, which could lead to scaling problems in the

ozone stage or later in the sequence. This is because one-third of the oxalic acid formed in the ozone stage is adsorbed by the pulp, despite good washing. The adsorbed oxalic acid is not released until the pH of the pulp is raised in a later stage. Taking this last 30% oxalic acid into account, it is clear that ozone is the bleaching agent giving rise to the most oxalic acid. **TJ**

Elsander is a research engineer at Stora Enso Research, Box 9090, 650 09 Karlstad, Sweden. Ek is an assistant professor in the Division of Pulp Technology, Royal Institute of Technology, 100 44 Stockholm, Sweden. Gellerstedt is a professor in the Division of Wood Chemistry, Royal Institute of Technology, 100 44 Stockholm, Sweden.

Stora Corporate Research is gratefully acknowledged for permission to publish these research results. The authors also acknowledge Mikael Öster for skillful experimental assistance.

Received for review July 2, 1998.

Accepted March 23, 1999.

LITERATURE CITED

- Krasowski, J. A. and Marton, J., *J. Wood Chem. Technol.* 3(4): 445(1983).
- Ulmgren, P., *Nordic Pulp Paper Res. J.* 12(1): 32(1997).
- Ulmgren, P., *TAPPI 1996 Minimum Effluent Mills Symposium Proceedings*, TAPPI PRESS, Atlanta, p. 17.
- Kratzl, K., Vierhapper, F., and Tengler, E., *Monatshefte Chem.* 106: 321(1975).
- Yamamoto, Y., Niki, E., Shiokawa, H., et al., *J. Org. Chem.* 44(13): 2137(1979).
- Kempf, A.W. and Dence, C.W., *Chemistry of Delignification with Oxygen, Ozone and Peroxides*, Uni Publishers, Tokyo, 1980, p. 207.
- Nilvebrant, N.-O. and Reimann, A., *Proceedings of 4th European Workshop on Lignocellulosics and Pulp*, Streza, Italy, 1996, p. 485.
- Johansson, M. H. and Samuelsson, O., *Carbohydr. Res.* 54: 295(1977).
- Buchert, J., Teleman, A., Harjunpää, V., et al., *Tappi J.* 78(11): 125(1995).
- Freiholtz, A., Master thesis (in Swedish), KTH, Stockholm, 1996.
- Gellerstedt, G. and Li, J., *Carbohydr. Res.* 294: 41(1996).
- STFI Method AH 83-12, "Oxalic acid, including calcium oxalate," STFI, Stockholm, 1996.