Capillary electrophoresis was applied for quantitative determination of sulfite, sulfate and thiosulfate in magnesium base bisulfite cooking liquor in the course of digestion. Separation was achieved based on the results of Gutleben with a buffer consisting of 5 mmol/L potassium chromate, pH 11.0, and 0.001% hexadimethrine bromide (HDB). For sampling under conditions of up to 150°C and 8 bar a water cooled six port valve was inserted into a bypass of the process stream. The samples were purged out with a mixture of sodium hydroxide and formaldehyde. Furthermore 0.01% hexadimethrine bromide was added to the samples. This method was properly validated in terms of calibration, limit of quantification, repeatability, linearity, accuracy and sample stability and was found to be suitable for general research purposes. Quantification was done by relation of the migration time corrected peak areas to an internal standard (chloride). Application of this method to several laboratory magnesium bisulfite cooking experiments revealed sulfite concentrations of 80 to 15 mg/mL showing a decrease during the cooking process and sulfate concentrations between 4 and 7 mg/mL showing a comparatively slight increase. Thiosulfate, however, was below the limit of detection of 0.3 to 0.7 mg/mL under standard conditions.

Keywords: cooking liquor, analysis, capillary electrophoresis, sulfite, sulfate

Introduction
Generally, quantitative knowledge about the course of the concentration of compounds in a process can be assumed to be helpful for its understanding and optimization regarding yield, recovery or costs. In the case of the magnesium base bisulfite process - an industrially applied method for the production of pulp - sulfur dioxide, sulfite, respectively, and other small inorganic anionic sulfur species derived from it in the cooking liquor are interesting objects for observation. In this work sulfite, sulfate and thiosulfate were investigated.

In the early stages of magnesium base bisulfite cooking titrimetric methods for the determination of their concentration are feasible but in the course of the delignification this is not possible any more due to the complex matrix consisting of degraded and solubilized organic compounds. To overcome this problem a separation step must be applied prior to quantification. From the analyst’s pool of separation techniques capillary electrophoresis (CE) was chosen, because there is no expensive stationary phase prone to fouling, which has to be expected in the case of chromatography or electrochromatography on dirty samples without tedious sample clean-up. In addition, fast separations in the range of a few minutes and even seconds are possible.

Capillary electrophoresis has become a widely accepted separation technique in quantitative analysis [1, 2]. There are several publications in the field of pulping [3 - 7], and also about the separation of anions in magnesium base bisulfite cooking liquor [8]. Separations in capillary electrophoresis are based upon different electrophoretic mobilities of the analytes in an
electrical field, which in turn are determined by size and charge of the analytes and properties of the background electrolyte, such as viscosity and permittivity. Besides the ion's own mobility there exists also the so called electroosmotic flow (EOF), which originates from charges on the surface of the capillary, caused for instance by deprotonation of silanol groups, derivatization or coating, leading to oppositely charged layers in the buffer. Upon application of an external electrical field the mobile one of these layers moves along the capillary dragging the whole contents in the direction according to this layer's charge. With the aid of the above mentioned modifications the analyst can control the direction and size of the EOF, which contributes to the ion's observed mobility by vector addition of EOF and the ion's own mobility. Fast separations will be possible if these two vectors possess the same direction. For anions this demands a positively charged capillary surface, which can be managed by adsorption of polymeric quaternary ammonium ions on the mostly used fused silica capillaries.

### Experimental

Based on the results of Gutleben [8] a capillary electrophoresis method was established for the quantitation of sulfite, sulfate and thiosulfate. A HP 3DCE instrument was used in the ce+P mode. The buffer consisted of 5 mmol/L potassium chromate adjusted to pH 11.0 with sodium hydroxide and 0.001 % hexadimethrine bromide (HDB) for the reversal of the EOF. The buffer was degassed by sonication and filtered through a 0.45 μm membrane filter. The separation occurred in a fused silica capillary of 60 cm length (51.5 cm effective length) and 50 μm diameter under the application of a voltage of –30 kV leading to a current of approximately 15 μA. Indirect UV detection was performed at 275 +/- 20 nm, the peak width was set < 0.01 min. Hydrodynamic injection was accomplished by 30 mbar and 10 s. The anions for calibration were used as their sodium salts. All substances were of p.a. grade, water was of HPLC grade. Between runs, the capillary was purged by a multistep sequence applying 0.1 mol/L sodium hydroxide, buffer without HDB and running buffer, but lately it was found that purging with running buffer at 2 bar and simultaneous application of a voltage of -30 kV for one minute was sufficient for repeatable results. The buffer (0.75 mL) was changed after six or less runs. For sampling under conditions of up to 150 °C and 8 bar a water cooled six port valve was inserted into a bypass of the process stream. The samples were purged out into a 10 mL volumetric flask containing sodium chloride solution as an internal standard with a mixture of sodium hydroxide (final 0.2 mol/L) for sulfur dioxide absorbance and formaldehyde (final 0.037 %) for prevention of sulfite oxidation. This sampling device is shown in Figure 1.

![Figure 1. Experimental set up for sampling.](image)

Furthermore, in a second dilution step with 0.037 % formaldehyde solution 0.01 % hexadimethrinic bromide was added to the samples to avoid capillary fouling by matrix effects. Finally samples were filtered through a 0.45 μm membrane filter. Standards for calibration were prepared accordingly with the addition of sodium chloride, formaldehyde and HDB. A blank solution additionally contained sodium hydroxide. A synthetic sample was prepared by weighing the substances in one flask and treating them correspondingly. The volume of the sample loop of the six port valve was determined by filling with a furfural solution of known concentration, purging it out into a 10 mL and 25 mL volumetric flask and determining the final concentration by HPLC. By doing so, it could be also confirmed that a final volume of 10 mL is sufficient for complete purging of the sample loop.
Results and Discussion

Typical electropherograms obtained with this method are presented in figure 2.

![Electropherograms](image)

**Figure 2.** Electropherograms of Standard (1) and Sample (2).

*Validation.* Generally, quantification was done by relation of the migration time corrected peak areas to an internal standard (chloride). Calibration was performed by triple injection of mixed standard solutions at four to six concentration levels and simple linear regression of the term \([\text{area (anion)} / \text{migration time (anion)}] / [\text{area (chloride)} / \text{migration time (chloride)}]\) versus concentration (anion) / concentration (chloride). During routine work calibration was done at three concentration levels by three or more injections throughout one batch. Linear calibration curves were obtained for sulfite (100 – 550 µg/mL, slope 0.9956, intercept -0.1735, \(r^2 0.998\)), sulfate (10 – 82 µg/mL, slope 0.7598, intercept 0.0034, \(r^2 0.999\)) and thiosulfate (10 – 100 µg/mL, slope 0.6029, intercept -0.0063, \(r^2 0.998\)). The linearity of the calibration curves was also successfully checked by plots of response factor versus concentration quotient, where no trends were visible and the response factors were all within 5 % of the average. The limit of quantification based on a peak height of nine times the noise was 55 µg/mL, 10 µg/mL and 10 µg/mL for sulfite, sulfate and thiosulfate, respectively. Thiosulfate was found to be absent at these concentrations under standard dilution in laboratory cooking experiments. Measurements of less diluted samples pointed towards concentrations in the range of 0.2 mg/mL of thiosulfate in undiluted laboratory cooking acid. Thus, no values for some validation tests were obtained for thiosulfate. Concentrations, which were calculated from observed peak areas during calibration, deviated 0.2 to 5.4 %, 0.3 to 6.7 % and 0.1 to 12.8 % from the true values for sulfite, sulfate and thiosulfate, respectively. The comparatively high value of thiosulfate was due to a point at the limit of quantification, at higher concentrations the deviation was less than 5.4 %. The repeatability of the instrumental measurement expressed as the relative standard deviation of 12 successive injections of a sample was 1.6 % and 2.9 % for sulfite and sulfate, respectively. The repeatability including sampling and sample preparation determined by six samples and single injection was 2.0 % and 3.6 % for sulfite and sulfate.
The linearity of sulfite and sulfate in the sample matrix in the range of the calibration was proven by taking a sample containing two loop volumes and preparation of five dilutions thereof covering the range of 50 to 250 % of the standard dilution. A plot of measured concentration of the diluted solutions versus dilution gave $r^2$ values of 0.999 and 0.998 for sulfite and sulfate, respectively. A plot of calculated concentration of the original sample versus dilution revealed a slight dependence of the result of sulfite on the dilution at low peak areas. However, all results were within 5 % of the overall average. In the case of sulfate no trends could be observed.

Accuracy was checked by spiking a sample before dilution up to twice the concentration of the untreated sample. Also thiosulfate, which was not detectable in the original sample, was added. Calculation of the recovery of these spiked samples yielded an average recovery of 96.2 %, 105.9 % and 104.4 % for sulfite, sulfate and thiosulfate, respectively. Comparison of capillary electrophoretic results and independent volumetric results of sulfite, which were routinely determined during the first stages of laboratory cooking experiments, showed an excellent correspondence of 100 % with a standard deviation of 4 %. A summary of these validation data is given in Table 1.

First experiments concerning the stability of untreated samples had revealed a 10 % increase of the sulfate and a corresponding decrease of the sulfite peak area after migration time and internal standard correction within six consecutive injections. Obviously some kind of protection against oxidation of sulfite had been required. Consequently, the suggested stabilization by addition of formaldehyde was checked by sevenfold injection of a sample containing 0.037 % formaldehyde and also some added thiosulfate in the course of 13 hours. The results showed a random scattering without any obvious trend. The relative standard deviations of 1.3 to 2.1 % were within an acceptable range proving the efficiency of the proposed stabilization method.
for the collection of one cooking experiment's diluted and stabilized samples and their batchwise analysis by CE afterwards. However, longterm storage, two weeks in a deepfreezer, was not successful.

Application. The above described and validated method was applied to several laboratory magnesium base bisulfite cooking experiments covering different kinds of wood, such as beech, eucalyptus and aspen, and several cooking conditions. Sulfite concentrations of 80 to 15 mg/mL showing a decrease during the cooking process and sulfate concentrations between 4 and 7 mg/mL showing a comparatively slight increase were found. Thiosulfate, however, was below the limit of detection of 0.3 to 0.7 mg/mL under standard conditions. Under less dilute conditions it was found to be present at about 0.2 mg/mL at the starting point of cooking and to decrease during the process. Figure 3 shows the course of concentrations of sulfite and sulfate during a typical magnesium base bisulfite cooking experiment.

Conclusion

A CE method for the quantitative determination of sulfite, sulfate and, with limitations, of thiosulfate in magnesium base bisulfite cooking liquor was validated and found suitable for general research purposes. However, precision could be improved and the linear range be extended. Nevertheless, the practical application to various laboratory cooking experiments was satisfactory.

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