ORIGINAL RESEARCH PAPER

Quantification of elemental sulfur in pulping liquors by thin-layer chromatography

Stefan Böhmdorfer[1] · Jakob Santner[2,3] · Antje Potthast[1] · Thomas Rosenau[1]

Abstract

The inorganic sulfur compounds that are used as pulping agents in the production of pulp and paper from wood are converted into a variety of sulfur species during processing. How sulfur is allocated to different streams and products in a pulp mill is relevant for efficient mill operation and to avoid harmful emissions. Pulping liquors are a highly challenging and potentially destructive sample matrix. We describe a thin-layer chromatographic method for the direct quantification of elemental sulfur in pulping liquors. The liquors are spotted (not sprayed!) directly onto the plate without prior purification, extraction, or workup. Sulfur is then eluted with *cyclo*-hexane and detected by densitometry at 285 nm or fluorescence quenching close to the solvent front. The method was validated for a calibrated range from 60 to 2000 ng sulfur on plate. The limit of detection was determined at 20 ng; measurement uncertainty was about 20%. With this method, 27–54 mg/L elemental sulfur were found in Kraft pulping liquors, which corresponds to 0.24–0.48% of the total sulfur in these samples.

Keywords Black liquor · Densitometry · Inductively coupled plasma–optical emission spectroscopy · Kraft pulping

1 Introduction

Sulfur-based salts—sodium sulfide in Kraft pulping and different sulfite salts in sulfite pulping—are the active reagents in the production of cellulosic pulps from wood. During the harsh and complex processes that isolate cellulose from wood, the employed sulfur salts are converted into various sulfur species of different oxidation states, which after the reaction coexist in the process lye, the so-called "black liquor." The black liquor is the aqueous extract that is obtained during the digestion of wood to obtain cellulose. It contains degraded and condensed lignin, hemicelluloses, degradation products of the polysaccharides, lipophilic wood extractives, and inorganic components, among them dissociated salts comprising the sulfur anions that are used in the process. Analyses that follow these sulfur-based ions through the process typically used capillary electrophoresis, and electrochemistry was also employed [1–4]. This has led to a better understanding of pulping processes in general, and helped to avoid unnecessary sulfur losses in pulp mills [5]. Formation of elemental sulfur, although known to occur, was studied only exceptionally [6]. Sulfur exists as several allomorphs, which are either small, cyclic molecules or polymeric chains. The most common one, *octa*-sulfur, can thermally decompose into smaller allomorphs during instrumental analysis, for example, in the inlet of a gas chromatograph, with negative consequences for the quality of the determined data [7]. The major obstacle for studies on elemental sulfur in pulping liquors is the simple fact that a suitable analytical system must both detect the target analyte and also resist the matrix of the sample, in this case the highly complex and corrosive pulping liquors. These are heterogeneous aqueous mixtures that contain lignin, carbohydrates, apolar extractives, and salts, sometimes at extremely alkaline pH. Most typically used equipment and separation columns are likely to be damaged by injecting pulping liquors without adequate workup beforehand. As a consequence, studies of pulping

✉ Stefan Böhmdorfer
  stefan.boehmdorfer@boku.ac.at

1 Department of Chemistry, Institute of Chemistry of Renewable Resources, University of Natural Resources and Life Sciences, Vienna (BOKU), Konrad-Lorenz-Straße 24, 3430 Tulln, Austria

2 Department of Crop Sciences, Institute of Agronomy, University of Natural Resources and Life Sciences, Vienna (BOKU), Konrad-Lorenz-Straße 24, 3430 Tulln, Austria

3 Institute for Plant Nutrition, Justus Liebig University Giessen, Heinrich-Buff-Ring 26─32, 35392 Gießen, Germany

liquors are usually limited to the total sulfur content determined by elemental analysis or the determination of sulfur anions [1, 3, 4].

To avoid damage to analytical equipment by matrix components, sulfur was isolated by liquid extraction. This was shown to be a feasible yet time-consuming approach [6]. Another option is to increase the robustness of the analytical instrumentation. Thin-layer chromatography (TLC) and its advanced sibling, high-performance thin-layer chromatography (HPTLC), were shown to be resistant to pulping liquors in the direct analysis of monosaccharides and the quantification of lignin [8, 9]. That TLC has the capability to detect *octa*-sulfur as a single peak without degradation has been shown for a range of challenging sample materials: thiourea, vulcanized rubber, lipids, and astronomical samples [10–14]. In addition, TLC and HPTLC are very resource efficient, since several samples are analyzed in parallel on one plate, and sample preparation is usually simple or not required at all. The analysis time per sample is often only a few minutes, and solvent consumption is a few hundred microliters.

We reasoned that the robustness of TLC would offer a good opportunity to quantify elemental sulfur in pulping liquors, which are matrices that are a challenge equal to those mentioned above. If a validated and robust method could be established, it would complement the existing analyses of ionic species.

2 Experimental

2.1 Samples

Stock standard solutions with 3000 µg/mL were prepared by dissolving 30 mg of sulfur ($\geq 99.5\%$, Sigma Aldrich/Merck, Darmstadt, Germany) in *cyclo*-hexane ($\geq 99.5\%$, Sigma Aldrich/Merck) in a 10 mL volumetric flask. Standard solutions of 1000, 300, 100, 30, and 10 µg/mL were prepared by diluting the stock solution. Black liquors from Kraft pulp mills were available from other projects and were selected arbitrarily. These samples were analyzed without sample preparation.

2.2 Thin-layer chromatography

The final method utilizes TLC aluminum sheets of 20×20 cm, silica 60, 200 µm layer thickness, without fluorescence indicator (order number 1.05553.0001, Merck) cut in half to 10×20 cm and predeveloped with methanol once before use. Other successfully tested plates comprise HPTLC and TLC silica with fluorescence indicator on glass plates from Merck (all 200 µm thick) as well as Sil G-25 glass plates from Macherey-Nagel (Düren, Germany).

Samples and standards were applied using an Automatic TLC Sampler 4 (ATS 4, CAMAG, Muttenz, Switzerland) with the following settings for 24 tracks per plate: contact application; dosage speed 250 nL/s; spot distance 7.5 mm; position of the first spot at 12 mm (*x* axis) and 8 mm (*y* axis). For standard solutions, 2 µL was applied per spot; the application volume for samples was 6 µL.

Development was carried out in a twin-trough chamber without chamber saturation or humidity control with 10 mL *cyclo*-hexane to a distance of 30 mm from the bottom of the plate. A horizontal development chamber can be used as well. After drying for several minutes at room temperature, the plates were documented using a visualizer (CAMAG) at white light and 254 nm in reflectance mode. For scanning densitometry, a Scanner 3 (CAMAG) was used with the following settings: detection wavelength 285 nm; scanning speed 20 mm/s; slit dimensions 5×0.2 mm, micro; data resolution 100 µm/step; sensitivity automatic; zero adjust at 12 mm (*x* axis) and 5.9 mm (*y* axis). All instruments were controlled using the software platform visionCATS 2.6 (CAMAG).

Quantification was based on peak areas. A Michaelis–Menten function with *y*-axis intercept was fitted to the areas of the standards that were co-developed on each plate.

For validation purposes, three separate stock solutions and dilution series were prepared and analyzed as described above on separate plates in quadruplicate. NeoLicy software (version 2.1.3) was used to evaluate calibration models and establish an accuracy profile after cross-validation that reflected recovery, bias, and the upper and lower limits of quantification at a β-expectation tolerance interval of 0.8, according to the recommendations of the Société Française des Sciences et Techniques Pharmaceutiques (SFSTP) [15–18].

For relative humidity studies, the six troughs of a Vario chamber (CAMAG) were filled with *cyclo*-hexane (saturated conditions), 4 Å molecular sieve (0% rH), as well as saturated aqueous solutions of lithium chloride (11% rH), magnesium chloride (33% rH), sodium bromide (58% rH), and sodium chloride (75% rH). The plate was mounted on the chamber, equilibrated for 20 min, and then developed with *cyclo*-hexane.

2.3 Total sulfur analysis by ICP−OES

Depending on sample availability, 1 or 2 mL liquor aliquots were pipetted into polytetrafluoroethylene (PTFE) digestion tubes, followed by 6.5 mL 65% HNO_3 and 1.5 mL 30% H_2O_2. The tubes were closed and the samples digested using a microwave-assisted digestion system (Mars 6, CEM, Kamp-Lintfort, Germany). Subsequently, the samples were diluted and analyzed for sulfur at 180.669 nm in axial mode on an Optima 8300 inductively coupled plasma–optical

emission spectroscopy (ICP–OES) instrument (Perkin Elmer, Waltham, MA, USA). Due to the lack of matrix-matched certified reference materials, and sulfur analysis on ICP–OES being prone to fluctuations in ionization rate in complex matrices, standard addition was performed on all samples at 300, 600, 900 mg/L; 50, 100, 150 mg/L; or 2, 4, 6 mg/L, depending on the sulfur concentration level of the liquor digest samples.

3 Results and discussion

3.1 Chromatography

Previously developed TLC methods for the determination of elemental sulfur were normal-phase separations with unmodified silica as the stationary phase; in some cases, mixtures of silica with magnesium silicate were used. Solvents were generally very apolar, comprising petroleum ether, *n*-heptane, hexanes, 2,2-dimethylbutane, and tetrachloromethane, in rare cases with polar modifiers [11–14]. We therefore based our method development on silica TLC plates and used the well-defined solvents *n*-heptane, *n*-hexane, *cyclo*-hexane (cHx), and toluene. Only neat solvents were considered, to avoid variation during the preparation of solvent mixtures in routine use. Petroleum ether, which is a mixture of hydrocarbons defined only by a boiling range, and the less common 2,2-dimethylbutane were also rejected as mobile phases. During this initial stage, TLC plates with fluorescence indicators were used. These allow the direct detection of elemental sulfur, which absorbs ultraviolet (UV) light. For all tested solvents, very high R_F values were observed for sulfur (0.94 for cHx, 0.88 for *n*-heptane) which eluted as a single peak without the undesired separation of the allomorphs that can be observed in other chromatographic techniques (Fig. 1, left, shows exemplary

chromatograms). The samples were applied without pretreatment, and it was found that sulfur eluted as predicted while other liquor components did not at all migrate in these very apolar solvents. Therefore, the short developing distance of 30 mm was chosen to save time, and sample pretreatment was found to not be required. As expected, chromatography was markedly slower for cHx: it took 200 s (3.33 min) to cover a developing distance of 30 mm compared with 86 s (1.43 min) for *n*-hexane. This seeming lack of speed is a minor issue in the light of the already very short effective developing times per sample: 8.3 s compared with 3.6 s. The shape and intensity of the obtained peaks was most defined when cHx was used for development. When *n*-hexane or toluene was used, spots were slightly paler and more diffuse and became indistinct with *n*-heptane. *cyclo*-hexane was therefore selected as eluent. TLC plates were selected as stationary phase to save costs, since the clear separation did not require a higher separation efficiency.

For the preparation of sulfur standard solutions, a range of apolar solvents is presented in the literature, including tetrachloromethane, chloroform, carbon disulfide, acetone, and hexane [11–14]. Also here, cHx was selected, since it gave the clearest and most intense bands and allowed to dissolve sulfur at concentrations higher than 1 mg/mL. Toluene even showed detrimental band broadening during application. In contrast to other separation methods, it is not a problem in TLC that the sample solvent–water–is immiscible with the solvent of the standards and the eluent–*cyclo*-hexane–since all solvents are evaporated before chromatography.

Sulfur absorbs light in the UV range. Consequently, we used plates with a UV-sensitive fluorescence indicator to detect it without derivatization during method development. Silver and rhodamine were initially tested as staining reagents. While both yielded reasonable first results, these options were not pursued further for the sake of simplicity, robustness, and resource efficiency. Instead,
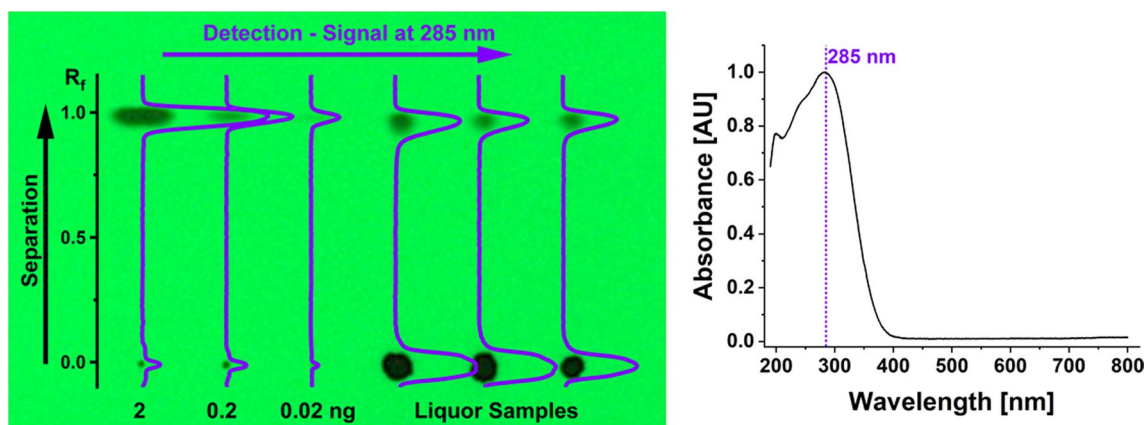

Fig. 1 *Left*: typical chromatograms of sulfur standards (applied amount indicated) and black liquor samples. The chromatograms recorded by densitometry at 285 nm are overlaid in purple. *Right*: UV/vis spectrum of elemental sulfur recorded off the TLC plate

we employed scanning densitometry for the direct detection of sulfur at a specific wavelength. The absorption maximum at 285 nm was confirmed by a spectral scan (see Fig. 1, right), and this wavelength was used for detection by scanning densitometry in all further analyses [10, 11, 13, 14]. With the direct detection by scanning densitometry, a fluorescence indicator in the stationary phase was no longer necessary, therefore running costs for the analysis were reduced by switching to aluminum-backed TLC-grade plates without fluorescence indicator. On these plates, peak shape and R_F of sulfur, as well as the immobility of the other liquor components remained as previously established during method development. Due to the short developing distance of 30 mm, the plates can be developed from either side or be trimmed after each separation to be used for two or three separations to increase resource efficiency. Care must be taken that the plates are cleaned by washing or pre-development with methanol before chromatography. Otherwise, contaminants that were adsorbed to the plate during storage and that elute in the solvent front can overlap with sulfur.

The application of a defined sample volume to the plate is fundamental for quantification and can be done by two methods: spraying or spotting. Spraying is generally preferred, as it gives sharp, homogeneous lines, which is beneficial for both resolution and quantitative evaluation. To our surprise, no sulfur was detected in liquor samples that were sprayed onto the plate. We did not investigate the cause for this, but suspect that the polymeric liquor components encapsulated sulfur in a process comparable to spray drying. Samples and standards were therefore spotted onto the plate. As an advantage, more samples can be fit onto one plate when spotting—24 instead of 15 spots at the chosen spraying settings—which reduced the effective analysis time per sample by 38%. Reproducibility of spotting was found to depend on the spotting speed: higher flow during spot application (200 and 250 nL/s) resulted in a smaller variation of peak area compared to lower flow (50 and 100 nL/s). Since this directly affects the precision of the calibration, the fastest setting was selected for sample application. Care must be taken to properly rinse the capillary that is used for sample application when changing from samples to standards, since the solvents of samples and standards—highly alkaline solutions and *cyclo*-hexane, respectively—are immiscible. For an automated system as the one used, it is recommended to rinse consecutively with water, 2-propanol, or acetone, and then with *cyclo*-hexane when changing from alkaline samples to sulfur standards. Although this adds to the time required for a full analysis, it can only be avoided by the less-precise manual sample application.

3.2 Quantification

Quantification was based on peak areas, since spotting liquor samples resulted in tailing peaks with varying height. For validation, three separate sets of standards in a range from 10 to 3000 µg/mL were analyzed in quadruplicate on three separate plates. First, a suitable calibration function was identified. Four established calibration models were applied to the validation measurements: a second order polynomial, a linear correlation of the square root of the peak area against the logarithm of the concentration, and Michaelis–Menten functions both with and without axis intercept [8, 19–21]. Only the Michaelis–Menten function with axis intercept passed the *F*-test at a confidence level of 0.95, while the Michaelis–Menten function without axis intercept narrowly failed the test. The polynomial could not model the lowest concentrations (10 and 30 µg/mL) and had its maximum within the calibration range at 2300 µg/mL. The logarithmic fitting function clearly failed the *F*-test. The selected calibration function was therefore a Michaelis–Menten function with axis intercept (see Fig. 2, left).

For validation, three separate stock solutions and dilution series were prepared that covered the range from 10 to 3000 µg/mL (20–6000 ng on plate). These solutions were each analyzed in quadruplicate; this allows taking into account the variations both within a plate and between plates. With this approach, it is possible to capture both accuracy (as mean bias, the average deviation from the expected value) and precision (as β-expectation interval, the interval that is expected to cover 80% of the future measurements) at each calibration level, and the cumulative influences of all analytical steps from the preparation of standards onwards are included (see Tables S1 and S2 in the Supplementary Material for the actual numbers). It became apparent (Fig. 2, right) that for the lowest level (10 µg/mL, 20 ng), sulfur could only be detected for some of the samples, and that at the highest level (3000 µg/mL, 6000 ng) the calibration yielded meaningless results. The validation was therefore limited to the range of 60–2000 ng on plate. At the lowest evaluated level, sulfur was reliably detected. The average bias of about −5% indicates an accurate evaluation, even though with limited precision. Therefore, 60 ng on plate can be assumed as the limit of quantification; the corresponding limit of detection would be placed at 20 ng, which is supported by the erratic detection of sulfur at 10 ng. The limit of detection and the limit of quantification are therefore between these values. The average bias then reaches about +20% at 200 ng and falls to −10% at the highest concentration. This behavior indicates that the calibration function, while it was the best of the investigated, passing a formal test and being commonly used, is still not optimal and introduces some systematic deviation. That the calibration points for 200 ng are slightly above the calibration curve can
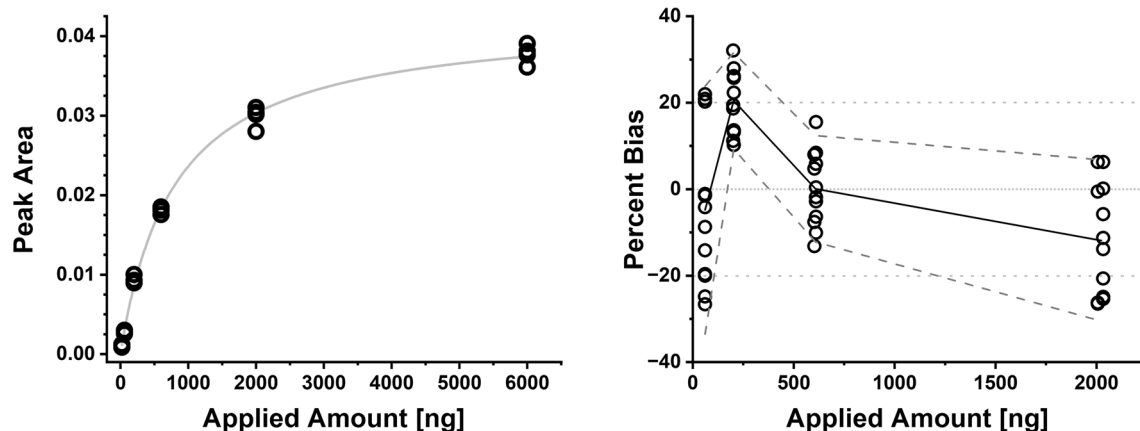
Fig. 2 *Left*: typical calibration curve for sulfur at 285 nm as recorded during method validation. *Right*: accuracy profile of the developed method. Circles denote the bias for each individual measurement. The black solid line indicates the mean bias, while the dashed gray lines indicate the upper and lower limits of the β-expectation interval. Lines at 0 and ±20% bias are provided for orientation

already be seen in Fig. 2, left. The determined β-expectation interval—it describes uncertainty, as 80% of all future measurements should fall into this interval—is below 20%, which is an acceptable value for this type of analysis. Based on this information, the method can be considered fit for the intended purpose.

3.3 Robustness

The developed method was found to be robust against most variations in separation conditions. The material of the stationary phase did not influence the elution of sulfur, as long as it was unmodified silica. Since resolution is not critical, TLC-grade silica can be chosen over its high-performance counterpart. Plates with fluorescence indicators can be used to detect sulfur directly at an increased limit of detection (LOD) of about 60 ng. However, prevalidation indicated a decreased sensitivity for densitometric quantification for plates with fluorescence indicators; therefore, plates without indicators were used. The solvent system consists of a single component, which avoids variations in composition caused by errors during preparation or lengthy storage. Based on the experiences made during method development, several apolar hydrocarbons besides *cyclo*-hexane (*n*-hexane, *n*-heptane, toluene) should give a useful separation. However, these solvents might reduce the quantitative performance. Separations were performed without chamber saturation, and identical results were achieved in regular (twin-trough) and horizontal TLC chambers. In agreement with theory, chamber saturation reduced the R_F value of sulfur from 0.94 to 0.56; at the same time, the development was accelerated [22]. The peaks obtained in saturated chambers were markedly broader than in unsaturated chambers, which can be expected to affect the LOD negatively. Relative humidity did not have an effect in the tested range (0–75%). It was essential to apply the samples by spotting, as spraying completely prevented *octa*-sulfur to elute from the application line. Precision was influenced by dosing speed, with faster speeds resulting in more reproducible peak areas and shapes. Prewashing the plates with methanol was crucial for quantitative analysis, as it removed compounds adsorbed to the plate, which might elute with the solvent front and overlap with the sulfur peak.

Resource consumption of this method is comparatively low due to the parallel analysis of several samples on each plate. At least 24 samples can be applied to each 20-cm-wide plate without interfering with each other. To develop a single plate, 10 mL of eluent and 103 min are required: sample application (84 min), development and drying (15 min), and detection (3 min). Thus, the analysis of each sample requires 0.42 mL of non-halogenated solvent and 4.3 min. Automatic sample application takes the most time, which includes an exchange of the machine's rinsing solvent from alkaline buffer over water and 2-propanol to *cyclo*-hexane. Some minutes might be saved by a manual application. Then, a solvent exchange is not necessary, but one must be aware that this will impair quantification. Given the short developing distance, a 10-cm-high plate can be used for up to three separate analyses (72 samples), if the used area of the plate is simply cut off after each analysis. No derivatization is necessary to visualize the target compound, if plates with fluorescence indicators are used.

3.4 Elemental sulfur in Kraft black liquors

Finally, the developed method was put into use. Nine black liquors were sampled from industrial Kraft processes. First, ICP−OES was used to determine the total amount of sulfur in the samples, which captures not only elemental sulfur but also different sulfur salts from pulping and bleaching,

organic sulfur compounds, such as dimethyl disulfide as well as sulfur bound to the released lignin. For this measurement, all organically bound sulfur is released during sample pretreatment by oxidative digestion. In these black liquors, the total sulfur content ranged from 8.6 to 13.3 g/L. The liquor samples were then analysed without pretreatment with the developed TLC method (see Fig. 3). Samples were analyzed in octuplicate on four different plates. The sample volume was increased to 6 µL to ensure that the applied amount of elemental sulfur was within the calibrated range. The observed concentrations in the black liquor were in the range of approximately 40–55 mg/L; only one sample ranged clearly lower at 27 mg/L (see Table 1). The uncertainty of the method was slightly larger than expected from validation, with a range from 13% to 45% and an average of 30%. In relation to the total mass of sulfur, elemental sulfur turned out to be a small fraction: typically, it made up 0.3–0.5% of the sulfur in black liquor, again with the exception of one single sample that only reached 0.24%. Generally, the portions of elemental sulfur were found to be around 0.4%, ranging from 0.24% to 0.48%.

4 Conclusions

Thin-layer chromatography proved to be a useful tool for the determination of elemental sulfur in black liquors. The method was intentionally kept as simple as possible: conventional TLC material is used, and the mobile phase consists of a single solvent. Consequently, the method is robust against variations in chromatographic parameters. Also, resource consumption is low at 4 min and 420 µL of eluent per sample. Sample preparation, for example liquid–liquid extraction, is not required. The sample must be spotted onto the plate and not sprayed. Detection of the

Table 1 Concentration of total sulfur (ICP−OES) and elemental sulfur (TLC) in Kraft pulping liquors

Sample	Total sulfur (g/L)	Elemental sulfur (mg/L) ($n=8$)	Mass percent elemental sulfur (%)	Relative standard deviation (%)
A	12.2	39.1	0.32	20
B	9.7	45.0	0.46	46
C	12.0	45.0	0.37	37
D	11.1	26.8	0.24	29
E	11.6	51.5	0.44	41
F	12.4	54.4	0.44	14
G	8.6	41.4	0.48	35
H	13.3	52.0	0.39	19
I	13.0	41.7	0.32	39

sulfur was possible in a single peak—unlike the fractionation into several peaks for example in gas chromatography (GC)—by UV densitometry at 285 nm without any derivatization. The use of nonfluorescent plates is beneficial for the detection of low amounts. A quantitative analysis of the sulfur content was possible based on the area of the detected peak. While the method is not highly precise, in part due to the residual lack-of-fit of the calibration function, it is fit for the intended purpose. The LOD was at about 20 ng sulfur on plate, and the calibrated range extended to 2000 ng.

In industrial black liquor samples from Kraft pulping, 27–54 mg/L elemental sulfur were found. These correspond to 0.24–0.48% of the total sulfur in these samples. The method is useful to trace sulfur in pulping liquors, which can help to retain it within the pulp mill to increase process efficiency and reduce emissions. In principle, the method can be combined with other thin-layer-based analyses of pulping liquors, for example, monosaccharide analysis or lignin content determination.
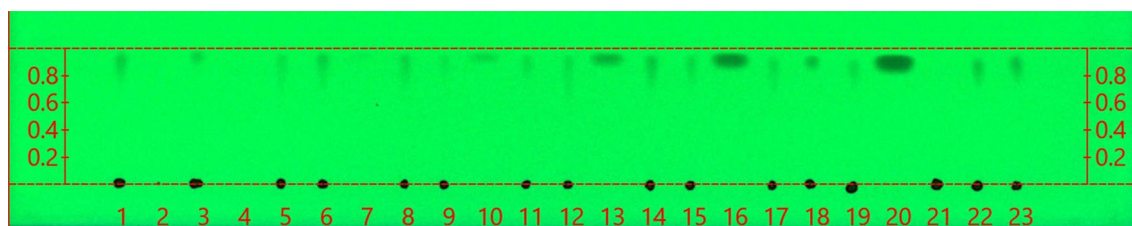

Fig. 3 Analysis of black liquors according to the established protocol. A plate with fluorescence indicator was used to visualize the sulfur for this graph. Standards are in lanes 2, 4, 7, 10, 13, 16, and 20

Declarations

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