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BSI Standards Publication

Fertilizers — Determination of complexed micro-nutrient ions in fertilizers — Identification of lignosulfonates

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The UK participation in its preparation was entrusted to Technical Committee CII/37, Fertilisers and related chemicals.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Foreword

This document (EN 16109:2011) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by May 2012, and conflicting national standards shall be withdrawn at the latest by May 2012.

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1 Scope

This document specifies two complementary methods (method A and method B) that allow lignosulfonates to be indentified as soluble complexing agents in fertilizers.

NOTE Lignosulfonate, as a complexing agent, is a natural polymer produced as a by-product of the sulfite method for manufacturing paper from wood pulp in the paper industry. As a natural polymer, it presents a poorly defined and variable chemical structure. It is an intricate mixture of small- to moderate-sized polymeric compounds with sulfonate groups attached to the molecule, and diverse complexing capacity.

The methods are applicable to EC fertilizers covered by Regulation (EC) No 2003/2003 [1].

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 1482-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

EN 12944-1:1999, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 1: General Terms*

EN 12944-2:1999, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 2: Terms relating to fertilizers*

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1:1999 and EN 12944-2:1999 apply.

4 Sampling and sample preparation

Sampling is not part of the method specified in this document. A recommended sampling method is given in EN 1482-1.

Sample preparation shall be carried out in accordance with EN 1482-2.

5 Method A: Determination of phenolic hydroxyl content and 232,5 nm absorption for the identification of lignosulfonates

5.1 Principle

The method for the determination of the phenolic hydroxyl content is based on the ultraviolet absorption of phenols in alkaline solution (phenolate). The absorbance of an alkaline solution of the sample is measured directly against an acid solution of the same sample. The phenolic hydroxyl content of the sample is calculated from the molar extinction coefficient maximum of the resulting curve and the molar extinction coefficient of reference compounds determined in the same way.

The determination of the absorption at 232,5 nm is normally considered the method for the quantification of lignosulfonates, providing that no other ultraviolet absorbing organic compounds are present.

NOTE For additional information see [3] and [4].

5.2 Apparatus

Usual laboratory equipment, glassware, and in particular the following:

5.2.1 Magnetic stirrer.

5.2.2 Balance, capable of weighing to an accuracy of 1 mg.

5.2.3 Filter paper for qualitative analysis, pore size 15 µm to 20 µm.[1]

5.2.4 pH-meter, equipped with a glass electrode.

5.2.5 UV-Vis spectrophotometer, equipped with 1 cm quartz cells.

5.3 Reagents

5.3.1 General

a) reagents shall be of recognized analytical grade;

b) water used for the preparation of sample solutions shall conform to EN ISO 3696, grade 2 and free of organic contaminants.

5.3.2 Hydrochloric acid solution, c(HCl)= 6 mol/l.

5.3.3 Sodium hydroxide solution, c(NaOH)= 0,1 mol/l.

5.3.4 Analytical grade fine mesh strong cation exchange resin [2]

Styrene/DVB type, 8 % crosslinked. Hydrogen form. Functional group: sulphonic acid. Nominal exchange capacity: 1,7 $mmol_{c/}ml$. Mesh: 50 to 100.

5.4 Procedure

5.4.1 Preparation of stock solution

Weigh, to the nearest 1 mg, 0,15 g to 0,20 g of the sample in a 100 ml beaker. Add 4 g of cation exchange resin (5.3.4) and about 20 ml to 25 ml of water. Allow the ion-exchange process to take place for 20 min, ensuring proper mixing by means of a magnetic stirrer.

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1) Albet 412 filter paper or equivalent is an example of suitable product commercially available. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

2) Biorad AG 50 W-X8 (50-100) Cat. No. 142-1431 is an example of suitable product commercially available. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

Filter (5.2.3) into a 250 ml volumetric flask to remove the resin and thoroughly wash the filter. Dilute to the mark with water (stock solution).

5.4.2 Solution A (acid)

Take an aliquot (40 ± 5 ml) of the stock solution into a 100 ml beaker and adjust pH between 2,0 and 2,2 with few drops of hydrochloric acid solution (5.3.2). Pipette 5 ml of the pH-adjusted solution into a 50 ml volumetric flask and dilute to the mark. Final concentration 0,06 g/l to 0,08 g/l.

5.4.3 Solution B (basic)

Pipette 5 ml of the stock solution into a 50 ml volumetric flask. Add 10 ml of sodium hydroxide solution (5.3.3) to adjust pH over 11,0. Dilute to the mark. Final concentration 0,06 g/l to 0,08 g/l. Check that the pH of the solution is over 11,0, if not prepare solution B adding more sodium hydroxide.

5.4.4 Solution C

Pipette 10 ml of the stock solution into a 100 ml beaker and fill with water to 60 ± 5 ml. Adjust the pH of the solution between 4,0 and 5,0 with the sodium hydroxide solution (5.3.3). Transfer quantitatively into a 100 ml volumetric flask, dilute to the mark with water and homogenize. See 5.4.6.

5.4.5 Measurement of phenolic hydroxyl content

Fill both cells in the UV spectrophotometer with water. Enter background correction. Scan from 340 nm to 220 nm to check baseline.

Fill the sample cell with solution B (5.4.3), and the reference cell with solution A (5.4.2). Scan from 340 nm to 220 nm. Rinse cells with water.

5.4.6 Measurement of 232,5 nm absorption

Fill the sample cell with solution C (5.4.4), and the reference cell with water and record absorbance at 232,5 nm. The absorbance of the final solution should be between 0,2 and 0,8 to minimize deviations from Beer's Law instrumental error. If necessary, the volume to be taken from stock solution (5.4.1) to prepare solution C (5.4.4) should be adapted.

5.5 Calculation

5.5.1 Phenolic hydroxyl content

Plot the spectrum in terms of absorbance. Record wavelength and absorbance for the maximum peak at 240 nm to 260 nm and for the minimum on either the right or the left side of the maximum. Subtract minimum absorbance from the maximum height (ΔAbs_{max}) (see Figure 1).

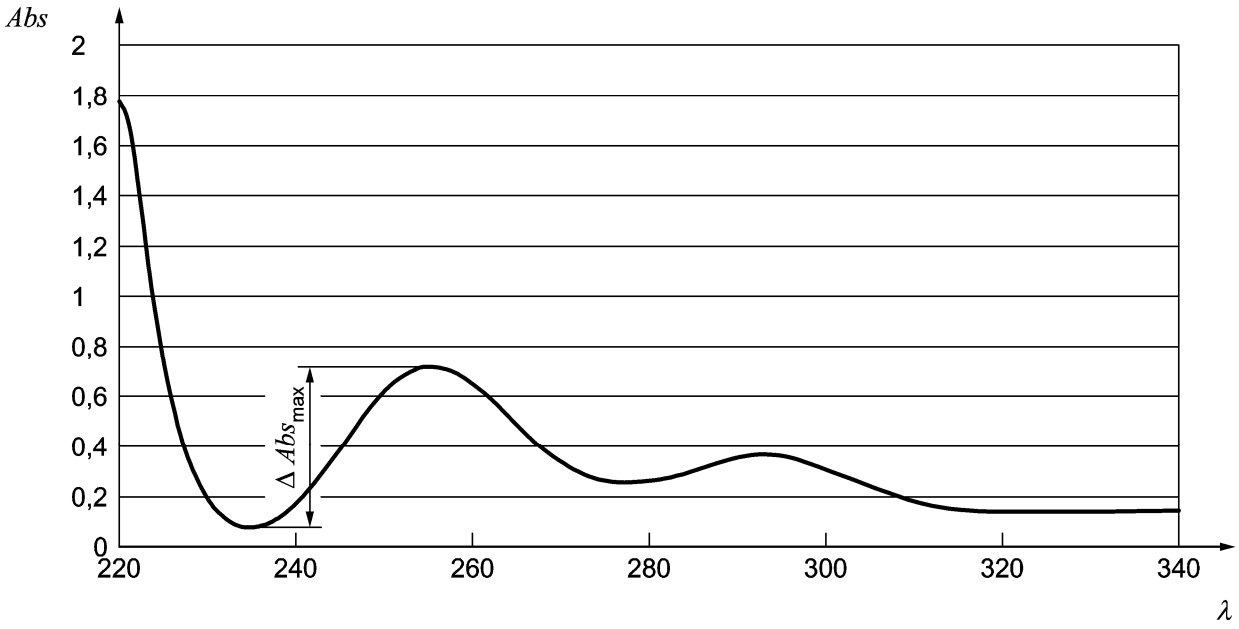

Figure 1 — Example of the spectrum of solution B against A for the determination of phenolic hydroxyl content of a lignosulfonate showing the maximum and the minimum (in this case at the left side) absorbances

Calculate the phenolic hydroxyl content, w_{ph}, of the sample, expressed as mass fraction in percent using the ΔAbs_{max} value of the sample and an average $\Delta\varepsilon_{max}$ value for reference compounds (8 867,5 l·mol^{-1}·cm^{-1}) by the following formula:

$$w_{ph} = \frac{\Delta Abs_{max}}{m} \times d \times 17 \times \frac{1}{\Delta\varepsilon_{max}} \times \frac{100}{1000} \quad (1)$$

$$d = \frac{50 \times 250}{5} \quad (2)$$

where

m is the mass of the test portion in grams;

d is the dilution factor included in 5.4.1, 5.4.2. and 5.4.3, in millilitres;

ΔAbs_{max} is the value obtained subtracting the minimum from the maximum absorbance;

17 is the number of OH mol $\frac{17\text{gOH}}{\text{molOH}}$;

$\Delta\varepsilon_{max}$ is the average molar extraction coefficient for reference compounds (8 867,5 l·mol^{-1}·cm^{-1}).

5.5.2 232,5 nm absorption as lignosulfonic acid content

Calculate the 232,5 nm absorption as lignosulfonic acid content, w_{la}, of the sample, expressed as mass fraction in percent, by the following formula:

$$w_{la} = \frac{A_{232,5} \times d}{m \times f \times 10} \quad (3)$$

$$d = \frac{100 \times 250}{V} \quad (4)$$

where

$A_{232,5}$ is the absorbance recorded at 232,5 nm (5.4.6);

m is the mass of the test portion in grams;

d is the dilution factor in millilitres considering dilutions in 5.4.1 and 5.4.4;

f is the absorptivity of the lignosulfonic acid in l/g cm, f = 36,5;

V is the volume in millilitres used to prepare solution 5.4.4.

6 Method B: Determination of organic sulfur content for the identification of lignosulfonates

6.1 Principle

Sulfur bound to the lignin backbone in lignosulfonate samples is commonly termed organic sulfur while the remaining sulfur is conveniently described as inorganic sulfur (free sulfur, bisulfite addition compounds, sulfates, sulfites, sulfides, thiosulfates and tetrathionates).

The method is based on the oxidation of inorganic sulfur to sulfate with alkaline iodine and its determination as barium sulfate. The remaining compounds are oxidized with a nitric-perchloric acid mixture to destroy organic matter and convert the sulfonated sulfur to sulfate, which is then determined as barium sulfate.

NOTE For additional information see [5].

6.2 Apparatus

Usual laboratory equipment, glassware, and in particular the following:

6.2.1 Magnetic stirrer.

6.2.2 Balance, capable of weighing to an accuracy of 0,1 mg.

6.2.3 Filter paper for qualitative analysis, pore size 15 µm to 20 µm.[3]

6.2.4 Ashless filter paper for quantitative analysis, pore size 2,5 µm.[4]

6.2.5 Porcelain crucibles, resistant to 800 ºC. The crucibles shall be calcinated at 800 ºC before use.

6.2.6 pH-meter, equipped with a glass electrode.

3) Albet 412 filter paper or equivalent is an example of suitable product commercially available. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

4) Whatman No. 42 filter paper or equivalent is an example of suitable product commercially available. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

6.2.7 Water bath or any other heating device.

6.2.8 Oven, (105 ±1) ºC.

6.2.9 Muffle furnace, 800 ºC.

6.3 Reagents

6.3.1 General

a) reagents shall be of recognized analytical grade;

b) water used for the preparation of sample solutions shall conform to EN ISO 3696, grade 2 and free of organic contaminants.

6.3.2 Sodium hydroxide solution, w(NaOH) = 10 %.

6.3.3 Hydrochloric acid, w 36 %-38 %.

6.3.4 Hydrochloric acid solution, c(HCl) about 6 mol/l.

Dilute 1 part of hydrochloric acid (6.3.3) with 1 part of water.

6.3.5 Potassium iodide

6.3.6 Iodine

6.3.7 Barium chloride solution, $w(BaCl_2)$ = 10 %.

If commercial solution is not available barium chloride solution can be prepared by dissolving 58,64 g of barium chloride dihydrate, $BaCl_2.2H_2O$, in water and diluting to 500 ml.

6.3.8 Nitric acid, w 64 %-66,5 %.

6.3.9 Perchloric acid, w 59 %-62 %.

WARNING — Perchloric acid is an oxidizing and corrosive substance, which by heating may cause explosion. Check SDS before use. In wet digestions with perchloric acid, treat the sample first with nitric acid to destroy easily oxidizable matter. Perchloric acid digestions and other procedures performed at elevated temperatures should be done in a specially designed perchloric acid fume hood.

6.3.10 Analytical grade fine mesh strong cation exchange resin [5]

Styrene/DVB type, 8 % crosslinked. Hydrogen form. Functional group: sulfonic acid. Nominal exchange capacity: 1,7 $mmol_c$/ml. Mesh: 50 to 100.

5) Biorad AG 50W-X8 (50-100) Cat. No. 142-1431 is an example of suitable product commercially available. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

6.3.11 Silver nitrate solution, 5 g/l.

6.4 Procedure

6.4.1 Preparation of 0,5 mol/l Iodine I_2 solution

Weigh 100 g of potassium iodide in a 250 ml beaker and dissolve in 150 ml of water. Weigh 31,73 g of iodine. Add it to the former iodide solution and dissolve it.

Transfer the solution quantitatively to a glass-stoppered amber-coloured 250 ml volumetric flask, add 5 drops of hydrochloric acid solution (6.3.4) and dilute to the mark with water.

6.4.2 Separation of inorganic sulfur

Weight, to the nearest 1 mg, 1 g of sample in a 100 ml beaker. Add 40 ml to 50 ml of water. If the sample is solid allow the complete dissolution.

Add 8 g of cation exchange resin (6.3.10). Allow the ion-exchange process to take place for 20 min ensuring proper mixing by means of a magnetic stirrer. Filter the solution through a filter paper (6.2.3) to remove the resin and thoroughly wash the filter. Collect the clear filtrate in a 250 ml Erlenmeyer flask, add 10 ml of sodium hydroxide solution (6.3.2) and allow to stand for 1 h at room temperature.

Add 10 ml of iodine solution (6.4.1) and leave standing 30 min more.

Dilute the solution to 200 ± 20 ml with water and adjust to pH 2 with hydrochloric acid solution (6.3.4).

Heat to 95 °C and add 10 ml of barium chloride solution (6.3.7). Stir well during the addition of barium chloride and continue stirring for additional 2 min. Let the solution over a water bath (6.2.7) for at least 2 h at 90 °C or in a heating device overnight at temperature ranging from 50 °C to 60 °C. This process will aid in the formation of larger crystals of barium sulfate. Then leave standing hot (60 ± 5) °C until the supernatant liquor is clear. Decant the clear solution through two slow ash-free filter papers (6.2.4) and then transfer the precipitate to the filter. Filter again the solution through the same two filters to ensure that all barium sulfate is retained. If precipitation is observed in the filtered solution it shall be filtered again through the same two filters until filtered solution is barium sulfate free. Wash the precipitate with 200 ml ± 20 ml of water and save the filtrate and washings into a 600 ml beaker.

NOTE Inorganic sulfur can be determined in this precipitate after ashing as in the determination of organic sulfur.

6.4.3 Determination of organic sulfur

Evaporate the filtrate in the beaker to 20 ml ± 5 ml.

Add 10 ml of nitric acid (6.3.8) and 10 ml of perchloric acid (6.3.9).

Cover with a watch glass and heat with intermittent swirling to white fumes of perchloric acid. Continue heating for 5 min.

Cool and add 5 ml of hydrochloric acid (6.3.3) and heat again to white fumes.

Cool, dilute to 200 ml, and adjust to pH 2 with sodium hydroxide solution (6.3.2). Barium sulfate crystals may already be present due to the excess of barium chloride added in the inorganic sulfur precipitation.

Precipitate the possible sulfate still in solution with barium chloride as follows. Heat to 95 °C and add 10 ml of 10 % barium chloride solution. Stir well during the addition of barium chloride and continue stirring for additional 2 min. Let the solution in the beaker covered by a watch glass to avoid evaporation over the water bath for at least 2 h at 90 °C or in a heating device overnight at temperature ranging from 50 ºC to 60 ºC to aid the formation of larger crystals of barium sulfate. Then leave standing hot (60 ± 5) °C until the supernatant liquor is clear. Decant the clear solution through two slow ash-free filter papers (6.2.4) and transfer the

precipitate to the filter. Filter again the solution through the same two filters to ensure that all barium sulfate is retained. If precipitation is observed in the filtered solution it shall be filtered again through the same two filters until filtered solution is barium sulfate free. Wash the precipitate with hot water (60 ºC to 70 ºC) until the washings are free of chloride. This can be checked by using silver nitrate solution (6.3.11). Place the filter paper and precipitate in a porcelain crucible (6.2.5) previously weighed to the nearest 0,1 mg. Dry in the oven (6.2.8) at 105 °C and introduce afterwards in muffle furnace (6.2.9). Set temperature to 200 ºC. After 15 min increase to 250 ºC. Let another 15 min and then rise the temperature to 800 ºC. When this temperature is reached, let stand for 1 h until complete ashing (6.2.9). Allow to cool in a desiccator and weigh to within 0,1 mg.

6.5 Calculation

Calculate the sulfur content, w_S, as a mass fraction in percent, taking into account the mass of the test portion and the barium sulfate precipitate according to the following equation:

$$w_S = \frac{m_1 \times 0{,}1374}{m_2} \times 100 \quad (5)$$

where

m_1 is the mass of $BaSO_4$, in grams;

m_2 is the mass of test portion, in grams;

0,137 4 is the ratio $\frac{\text{MWS}}{\text{MWBaSO}_4}$.

7 Expression of the results

7.1 Relative phenolic hydroxyl content

Calculate the relative phenolic hydroxyl content, w_{Rph}, in the fertilizer, expressed as a mass fraction in percent according to the following equation:

$$w_{Rph} = \frac{w_{ph}}{w_{la}} \times 100 \quad (6)$$

where

w_{ph} is the phenolic hydroxyl content in percent;

w_{la} is the lignosulfonic acid content in percent.

The results are expressed as a percentage with one decimal place.

The value of the lignosulfonic acid content shall be the mean of the values obtained in 5.5.2 as procedures A and B do not share initial solutions.

NOTE A percentage of $w_{Rph} \geq 1{,}5$ % has been described for fertilizers containing lignosulfonates.

7.2 Relative organic sulfur content

Calculate the relative organic sulfur content, w_{RS}, expressed as a mass fraction in percent in the fertilizer according to the following equation:

$$w_{RS} = \frac{w_S}{w_{la}} \times 100 \quad (7)$$

where

w_S is the sulfur content in percent;

w_{la} is the lignosulfonic acid content in percent.

The value of the lignosulfonic acid content shall be the mean of the values obtained in 5.5.2 as procedures A and B do not share initial solutions.

NOTE A percentage of $w_{RS} \geq 4{,}5$ % has been described for fertilizers containing lignosulfonates.

8 Precision

8.1 Inter-laboratory test

A first inter-laboratory test was carried out in 2008 with eight participating laboratories and three different samples: one non-commercial, Zn lignosulfonate, one commercial, Fe lignosulfonate and one commercial micronutrient complex, not lignosulfonate. The reproducibility results were poor, especially those corresponding to Method B (organic S content). A second inter-laboratory test was performed in 2009 with eight participating laboratories from four countries and three different samples. The samples were the same as the ones of the first ring test except for the Zn lignosulfonate, and a commercial Zn lignosulfonate was chosen. For this test some modifications were included in the method. The results of this inter-laboratory test are summarized in Annex A.

Repeatability and reproducibility were calculated according to ISO 5725-2.

8.2 Repeatability

The absolute difference between two independent single test results, obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will in not more than 5 % of the cases exceed the values of r given in Table 1.

8.3 Reproducibility

The absolute difference between two single test results, obtained with the same method on identical test material in different laboratories by different operators using different equipment, will in not more than 5 % of the cases exceed values of R given in Table 1.

Table 1 — Mean values, repeatability and reproducibility limits

Sample	$\bar{x}$ %	r %	R %
Relative phenolic hydroxyl content (%)			
S1 Zn-LS	1,88	0,41	0,47
S2 Fe-LS	1,95	0,54	0,87
S3 No LS	0,00	0,00	0,00
Relative organic sulphur content (%)			
S1 Zn-LS	5,38	1,32	2,01
S2 Fe-LS	4,62	1,53	2,64
S3 No LS	3,46	5,55	7,71

9 Test report

The test report shall contain at least the following information:

a) all information necessary for the complete identification of the sample;

b) test method used with reference to this document;

c) test results obtained;

d) date of sampling and sampling procedure (if known);

e) date when the analysis was finished;

f) whether the requirement of the repeatability limit has been fulfilled;

g) all operating details not specified in this document, or regarded as optional, together with details of any incidents occurred when performing the method, which might have influenced the test result(s).

Annex A
(informative)

Statistical results of the inter-laboratory test

A.1 General

The precision of the method has been determined in the year 2009 in an inter-laboratory trial with eight laboratories participating and carried out on three samples of fertilizer. The statistical results are given in Table A.1. and A.2.

A.2 Test Samples

Three different samples were provided to all the participants, two solid fertilizers and one liquid solution:

— Sample 1 Zn-LS: one Zn lignosulfonate (solid)

— Sample 2 Fe-LS: one Fe lignosulfonate (liquid)

— Sample 3 No LS: one micronutrient complex, not lignosulfonate (solid)

Sample 3 was included in order to determine the performance of the method to differentiate lignosulfonate from other complexing agents.

A.3 Inter-laboratory test procedure

The participant laboratories were requested to perform three replicates of each sample according to the proposed method. The parameters measured were: phenolic OH (%), lignosulfonic acid (%), relative phenolic OH (%), organic S (%) and relative organic S (%). Two decimals were specified for each determination.

The test samples were sent to ten laboratories from five countries.

Eight laboratories from four countries presented results, but only five laboratories from three countries presented a complete set of results.

Test results, observations and remarks were reported.

A.4 Results and statistical interpretation

Statistical calculations were run on all the results, according to ISO 5725-2:1994.

Parameters of repeatability and reproducibility were evaluated for each sample (mean value, standard deviation of repeatability, standard deviation of reproducibility, repeatability, reproducibility, relative standard deviation of repeatability and relative standard deviation of reproducibility). The statistical results are given in Table A.1 (method A) and Table A.2 (method B).

Table A.1 — Statistical results of the interlaboratory test. Method A

Parameter	Phenolic OH w_{ph}			Lignosulfonic acid w_{la}			Relative OH w_{Rph}		
	Sample			Sample			Sample		
	S1 Zn-LS	S2 Fe-LS	S3 No LS	S1 Zn-LS	S2 Fe-LS	S3 No LS	S1 Zn-LS	S2 Fe-LS	S3 No LS
Number of laboratories	5	5	5	6	6	6	5	5	5
Number of outliers	0	0	1	1	0	0	0	0	1
Number of laboratories after elimination of outliers	5	5	4	5	6	6	5	5	4
Mean value, %	0,77	0,31	0,00	41,24	16,84	5,16	1,88	1,95	0,00
Repeatability Standard Deviation, s_r %	0,06	0,04	0,00	0,77	0,64	0,62	0,15	0,20	0,00
Repeatability limit, r %	0,16	0,10	0,00	2,14	1,78	1,71	0,41	0,54	0,00
RSD_r %	7,7	11,6	-	1,9	3,8	12,0	7,9	10,1	-
Reproducibility Standard Deviation, s_R %	0,06	0,04	0,00	1,14	2,45	3,26	0,17	0,32	0,00
Reproducibility limit, R %	0,17	0,10	0,00	3,16	6,77	9,04	0,47	0,87	0,00
RSD_R %	7,8	11,6	-	2,8	14,5	63,3	9,0	16,2	-

Table A.2 — Statistical results of the interlaboratory test. Method B

Parameter	Organic S w_S			Relative organic S w_{RS}		
	Sample			Sample		
	S1 Zn-LS	S2 Fe-LS	S3 No LS	S1 Zn-LS	S2 Fe-LS	S3 No LS
Number of laboratories	6	6	6	5	5	4
Number of outliers	1	0	2	1	0	0
Number of laboratories after elimination of outliers	5	6	4	4	5	4
Mean value %	2,28	0,74	0,07	5,38	4,62	3,46
Repeatability Standard Deviation, s_r %	0,20	0,09	0,03	0,47	0,55	2,01
Repeatability limit, r %	0,55	0,26	0,08	1,32	1,53	5,55
$RSDr$	8,7	12,7	38,7	8,8	11,9	57,9
Reproducibility Standard Deviation, s_R %	0,31	0,15	0,08	0,73	0,95	2,79
Reproducibility limit, R %	0,85	0,41	0,22	2,01	2,64	7,71
RSD_R %	13,4	20,3	106,6	13,5	20,7	80,4

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