

EXAMINATION OF THE CONTENT OF SUBSIDED MATERIALS IN ENVIRONMENTAL WATER

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Summary: *This paper presents the results of determining the performance characteristics of the test method SRPS EN 872: 2008 in one laboratory and their compliance with the relevant requirements, ie the assessment of the laboratory's ability to use the test method for the intended purpose.*

The performance characteristics of the method indicate the ability of the laboratory to deliver test results with acceptable reliability for the intended use of the results, for example: assessment of compliance with the provisions of the regulations. The detection limit indicates the minimum values that can be measured with a specific test method; the limit of quantification indicates the minimum values that can be measured with known and acceptable measurement uncertainty. The accuracy and precision of the test method are the main components of measurement uncertainty as a quantitative measure of the quality of the test method.

Key words: *Laboratory tests, test methods, verification of test methods, accuracy, detection limit and quantification, measurement uncertainty, water, suspended matter, water quality.*

1. INTRODUCTION

For any type of test, a suitable test method must be used. Suitability is reflected in the benefits for a specific purpose, and it is proved by determining the characteristics of performing the test method (performance of the method) and by comparing the determined characteristics with the requirements for the intended use. For example, if the limit of quantification is sufficiently low for the intended purpose, if the quantitative limit of the method is 0.1 mg / l and the maximum allowed value is 0.05 mg / l, the method is not suitable. If the accuracy of the method is 1mm, and it is necessary to measure the dimensions of 0.1mm, the method is not suitable. If the maximum tolerance of a certain feature is $\pm 3\%$, and the accuracy of the method is $\pm 5\%$, the method is not suitable.

For standard test methods, eg ISO, EN, ASTM, EPA,... or methods published by a reputable professional or scientific organization, the suitability for the intended use has been demonstrated, however, each laboratory must demonstrate its ability to carry out the test method before starting the test method with acceptable characteristics of performance (precision, accuracy, detection limit and quantification ...). Demonstration is called method verification in the laboratory.

The goal of this paper is to present the results of determining the performance of the test method SRPS EN 872: 2008 in one laboratory and their compliance with the relevant requirements, or the assessment of the laboratory's ability to use the test method for the intended purpose.

2. SUSPENDED MATTER IN THE WATER

The content of suspended matter in the water indicates the quality of water, generally, the lower the content of the suspended matter in the waters, the less polluted they are. Water quality is defined by regulations. The content of suspended matter is one of the parameters of the division into the surface water quality class, the categorization of watercourses, the maximum permissible value for the suspended matter is defined for certain types of wastewater.

The suspended matter is a tiny scattered insoluble part of matter in water and consists of: clay particles, sludge particles, fine, fine organic and inorganic matter, microorganisms and other small living organisms, plankton and so.

Suspended materials are more or less stable suspensions that can be easier and harder than water and can be separated into the bottom or spilled onto the surface over time; theoretically: suspended matter is precipitated in a calm water; practically: precipitated suspended matter are those that precipitate in two hours. They occur in many wastewaters, waters spilling the surface of the earth, and as such they reach the watercourses and pollute them. A certain part of the suspended matter does not precipitate or survives in the waters and in the long period of time, stability is different for different types of pollution, unstable contaminated waters are those that contain a large amount of suspended matter, especially of organic origin, while water with few suspended matter can be characterized as stable. Suspended substances occur: due to human activities, from: urban wastewater, industrial wastewater and diffused sources (agricultural activities, logging, from development of urban areas...) as a result of natural processes of washing from the surface of the earth.

A suitable method of testing the content of suspended matter is that method whose limit of quantification is lower than the lowest value of interest, from the point of view of the regulation that is the lowest allowed value.

There is a standard method published in Serbia at the Institute for Standardization of Serbia as SRPS EN 872: 2008, Water quality - Determination of suspended particulate content - Filtration method through glass fiber filters. The method defines the performance characteristic of the maximum allowable value for repeatability.

Each laboratory must confirm the ability to perform the test method in accordance with the criteria defined by the test method, regulations and standards of interest and/or good laboratory practice for the said area and test technique. Laboratories are accredited for water testing in accordance with applicable regulations.

Table 1 gives data for surface waters in accordance with the Regulation on the limit values of polluting substances in groundwater and sediment and deadlines for their reach (Official Gazette of RS, No. 50/2012).

Table 1. Limit values of polluting substances in groundwater

Parameter	Unit of measure	The limit values				
		Class I	Class II	Class III	Class IV	Class V
Suspended matter	mg/l	25	25	-	-	-

Table 2 gives the limit values for the emission of waste water from the facility and plants for processing fruits and vegetables in accordance with the regulation on limit values of emissions of pollutants in the water and the deadlines for their completion (Official Gazette of the Republic of Serbia No. 67/2011) and 1/2016).

Table 2. Limit values for the emission of waste water from the facility and plants

Parameter	Unit of measure	Emission limit value
Suspended matter	mg/l	35

The regulation on the method and conditions for measuring the quantity and testing of the quality of wastewater and the content of the report on the performed measurements ("Official Gazette of the Republic of Serbia", No. 33/2016) define the reference methods for conducting the monitoring of wastewater.

Table 3. Reference methods for conducting wastewater monitoring

Name of the parameter	Reference method	Method description
Suspended matter	SRPS EN 872:2008 SRPS H.Z1.160:1987	Filtration through glass fiber filters, Gravimetric

3. BRIEF STATEMENT OF THE METHOD SRPS EN 872: 2008, WATER QUALITY - DETERMINATION OF SUSPENDED PARTICULATE CONTENT - FILTRATION METHOD THROUGH GLASS FIBER FILTERS

Field of application

Surface and wastewater, by the method defined minimum quantification 2 mg / l

Principle:

Gravimetric method, the result is the difference in the filter mass after and before vacuum filtration of the water sample and filter drying at 105 ° C.

Equipment:

Membrane filtration system,

Dryer,

Analytical scale, 0.1 mg resolution,

Petri cups for receiving filters during transport and drying,

Normal sampling sizes or suitable sensors with the accuracy of the reading division, maximum 2% of the measured volume (for example, if 150 ml of sensors are measured, it must have a maximum of 3 ml).

Filters:

From glass pine silicate fibers, round corresponding diameter (47-50 mm),

Reagents:

Control reference suspension, 1L: Microcrystalline cellulose (pre-dried at 105 ° C for one hour), 50 mg / l immediately before use, to be made directly in distilled water.

Microcrystalline cellulose, extra pure, LOT A0343740, CAS 9004-34-6, Code 382312500, particle size 90 µm, manufacturer ACROS ORGANICS.

Sample handling:

Take a sample of water in a transparent 1l bottle; leave a little space at the top to shake. Perform the test as quickly as possible, maximum 4 hours after sampling. Otherwise keep at T 1 ° C to 5 ° C, maximum 2 days.

Procedure:

Heat the filter paper at 105 ° C for one hour in the oven in an open petri dish, cool it in a desiccator, measure it on the analytical balance, measure at least twice, until the differences between consecutive measurements are not less than 0.3 mg for a 47-50 mm filter (maximum allowed for a blank test).

Balance the temperature of the water sample with the temperature in the laboratory.

Take a suitable volume of the sample depending on the expected value, preferably the weighing difference before and after filtration is between 5 and 50 mg, if the difference is less than 5 mg, repeated with a higher volume. Typically, the volume is between 100 and 500 ml, for 1 l of pure water. Volumes greater than 1l should be avoided.

Place the filters in the filtration system, shake the sample well and immediately slide one tilt into the filter system funnel. Filter by vacuum, rinse the vessel with 20 ml of distilled water and rinse the filter with another 20 ml without turning off the vacuum, completely dry the vacuum filter.

Usually, the filtration is completed in a few minutes, if the filter is congested, repeat with a smaller volume.

Remove the filter from the system with tweezers, take care not to damage, transfer to the petri dish and transfer to the dryer at 105 ° C, dry for a minimum of 1 hour, max. 14 hours. Remove from the dryer, cool in a desiccator and weigh as before filtration.

Calculation, $x = 1000 (b-a) / V$, x-mg / l suspended matter, b-mass of the filter after filtration, filter a-mass before filtration, V volume of the sample in ml.

Quality control of the test method: In a series of measurements (once a day when real samples are measured)

- Reference sample suspension of 50 mg / l
- Sample implication (split sample into two samples after shaking, just before the start of the test),
- Blunt test - demineralized water, the criterion defined by the test method, less than 2 mg / l

Admission Criteria for a duplicate sample of max 10% (based on data from the method and verification experiment).

4. REQUIREMENTS CONCERNING THE PERFORMANCE CHARACTERISTICS OF THE TEST METHOD

To determine the content of the suspended particles, two types of requests appear;

1. Requirement expressed in the test method SRPS EN 872: 2008: detection limit less than 2 mg / l (as the maximum value of the blank test) and
2. Requests stated in the Regulation on Limit Values of Emissions of Polluting Substances in Water and Time Limits for Their Completion (Official Gazette of the Republic of Serbia No. 67/2011, 48/2012 and 1/2016),

All standardized methods that meet the requirements can be applied to determine the pollutants listed. Table 4 shows the requirements to be followed when selecting an analytical method for analyzing pollutants in wastewater.

Table 4. Requirements to be followed when selecting an analytical method for analyzing pollutants in wastewater.

Parameter	% Correctness of parameter value ^(I)	% Of the accuracy of the parameter value ^(II)	% Limit of detection of parameter value ^(III)
Total suspended matter	15	15	15

^(I) Correctness is a systematic error and represents the difference between the mean values of a large number of repeated measurements of the true value.

^(II) Precision is an accidental error and is expressed as a standard deviation of the results around the mean value. A double standard deviation is acceptable.

^(III) The detection limit is either:

- Three times the relative standard deviation of the natural sample with a low concentration of the parameter, or
- five times the relative standard deviation of the blank test.

Good laboratory practice requirement for gravimetric measurements after curing and evaporation of solvents:

- A precision as the maximum difference between two consecutive tests of 10%
- Accuracy of 90-110% of the previously determined exact value

5. PROCEDURE FOR DETERMINING THE DETECTION LIMIT AND LIMITS OF QUANTIFICATION

Demineralized water was used to investigate the LOD detection limit and limit quantification LOQ, in which the content of the suspended matter was close to zero. Six consecutive determinations of suspended matter in a 500 ml sample were performed and the values obtained are shown in Table 5:

Table 5. Sample: Demineralized water

Test number	Mass of the container with filter paper before filtration (g)	Mass of the container with filter paper after filtration (g)	Suspended matter (mg/l)
1	119.2547	119.2549	0.40
2	114.9632	114.9633	0.20
3	115.8214	115.8214	0.00
4	132.8624	132.8626	0.40
5	117.3685	117.3686	0.20
6	119.2546	119.2549	0.60
7	117.7712	117.7714	0.40
8	111.4557	111.4559	0.40
9	116.4558	116.4559	0.20
10	120.8533	120.8536	0.60
Stdev (mg/l)			0.19

6. DISCUSSION OF THE OBTAINED TEST RESULTS

The resulting limit of quantification meets the requirements of the test method of 2mg / l. If the maximum permissible value for the first class of water of 25 mg / l is the lowest value of interest, the detection limit (0.95 mg / l (Table 6), as the five-fold value of the standard deviation) is 3.8% of the lowest value of the parameter of interest which meets the requirements of a maximum of 10% stated in the Regulation on limit values for emissions of pollutants in water and deadlines for their achievement (Official Gazette of the Republic of Serbia no.67 / 2011, 48/2012, and 1/2016).

Table 6. Limit values for emissions of pollutants in water

Detection limit as a triple standard deviation of test results. A sample with suspended matter values close to zero	0.57mg/l
Detection limit as a five-standard standard deviation of test results. A sample with suspended matter values close to zero	0,95mg/l
Detection limit as a ten-standard standard deviation of test results. A sample with suspended matter values close to zero	1.9 mg/l

7. A PRECISION DETERMINATION PROCESS

To determine the precision, a natural wastewater sample was used (Table 7), with the values of suspended matter several times the limit of the quantification method and the quality control sample -control reference suspension, microcrystalline cellulose 50mg / l.

Table 7. Natural wastewater sample

No.	Mass of the container with filter paper before filtration (g)	Mass of the container with filter paper after filtration (g)	Suspended matter (mg/l)
1	124.0563	124.0872	61.80
2	117.2856	117.3159	60.60
3	128.3547	128.3858	62.20
4	117.3682	117.3984	60.40
5	115.7457	115.7762	61.00
6	118.3564	118.3879	63.00
Stdev (mg/l)			1.01
Mean value (mg/l)			61.50
Stdev rel(%)			1.64%

Repeatability as the maximum difference between two consecutive repetitions is $2.7 * Std = 2.7 * 1.01 = 2.7 \text{ mg / L}$,

Repeatability expressed as relative value in relation to the found (average determined) % = 4,4%,

Values for the control sample of microcrystalline cellulose 50 mg / L, obtained in 21 days, daily by two tests (Table 8)

Table 8. Values for the control sample of microcrystalline cellulose

1.	45.2	15.	48	29.	51
2.	48	16.	48.5	30.	50.5
3.	45.8	17.	47.3	31.	49.5
4.	48.5	18.	50.5	32.	50.5
5.	48	19.	51	33.	49.35
6.	46.7	20.	48.5	34.	50
7.	47.3	21.	46.1	35.	49.35
8.	49.3	22.	46.1	36.	46
9.	50	23.	46	37.	49
10.	51	24.	46.5	38.	49.3
11.	49.4	25.	46.25	39.	50
12.	49.9	26.	47.7	40.	50
13.	50.5	27.	49	41.	47.7
14.	48	28.	52	42.	45.2

Characteristic values for performed measurements (Table 9) obtained by statistical processing of measurement data.

Table 9. Characteristic parameters of microcrystalline cellulose test

Mean value of measurement,	48.53	mg/l
Accuracy, as a percentage of the determined value	97%	
Standard deviation	1.73	mg/l
Standard deviation	3.6%	
Bias	2.9%	

Repeatability as a double standard deviation is $2 * 1.73 = 3.5 \text{ mg / l}$, Repeatability as the maximum difference between two consecutive repetitions is $2.7 * Std = 2.7 * 1.73 = 4.67 \text{ mg / l}$, or 9.6% of the correct value. Based on the examination of the natural sample of waste water and the control sample, a

repeatability of 10% of the obtained test result in the long term is adopted (the maximum allowed difference between the two test results).

If the maximum permissible value for the first class of 25 mg / L water is taken as the lowest value of interest, the accuracy (3.5 mg / l, as the double standard deviation value) is 14% of the lowest value of the parameter of interest. Which satisfies the requirement of maximum 15% stated in the Regulation on limit values of emissions of pollutants in the water and the deadlines for their completion (Official Gazette of the Republic of Serbia No.67 / 2011 48/2012 and 1/2016), as well as in the general criteria for determination of individual contaminants in wastewater.

8. PROCEDURE FOR DETERMINING ACCURACY

To determine the accuracy of the results used:

- For quality control sample - control reference suspension, microcrystalline cellulose 50 mg / L

Table 10. Accuracy of measurement of microcrystalline cellulose

Mean value of the laboratory from 40 determinations	The exact value of the control material	Accuracy (as a percentage of the correct value)	Bias	Bias
48,53 mg/l	50mg/l	97%	1,47 mg/l	2.9%

-For a sample from the International Laboratory Testing Scheme, LGC AQUACHECK Proficiency Scheme AQ2506, round 503, April 2016, suspended solids

Table 11. Accuracy of Laboratory Testing

The result of the laboratory	Exact value from the testing scheme	Accuracy (as a percentage of the correct value)	Bias	Bias
37.8 mg/l	36.9 mg/l	102.4%	0,9 mg/l	2.4%

Accepted ratio of the test method is 95% to 105%.

If the maximum permissible value for the first class of water is 25 mg / l as the lowest value of interest, the correctness (1.47 mg / l, as the difference between the mean values of a large number of repeated measurements of the true value) is 5.9% of the lowest value parameter of interest. Which meets the requirement of a maximum of 15% as stated in the Regulation on limit values of emissions of pollutants in water and deadlines for their reach (Official Gazette of the Republic of Serbia No. 67/2011, 48/2012 and 1/2016).

9. CONCLUSION

Performance characteristics of the test method (performance of the method) in the laboratory (detection limit, limit of quantification, repeatability and accuracy) meet the defined requirements:

In the reference document SRPS EN 872: 2008,

In accordance with the current regulation, the Regulation on limit values of emissions of pollutants in water and deadlines for their completion (Official Gazette of the Republic of Serbia No. 67/2011, 48/2012 and 1/2016), as well in the General criteria for determining individual pollutants in wastewater

As a good laboratory practice for gravimetric methods after filtering and evaporation of the liquid phase of the sample.

Laboratory may use method SRPS EN 872: 2008, Water quality - Determination of suspended particulate matter content - Filtration method through glass fiber filters to control the quality of surface and groundwater according to applicable regulations.

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