Assessment of the Accuracy of Analyzers for Automatic Determination of PM$_{10}$ and PM$_{2.5}$ Particulate Matter in Ambient Air

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The paper presents the test results regarding the evaluation of the accuracy of the PM$_{2.5}$ and PM$_{10}$ particulate matter concentration measurement performed with the uRADMonitor A3 fixed air quality monitoring station produced by SC MAGNASCI SRL. The procedure involves the calculation of the accuracy elements: trueness and precision, based on the experimental data obtained by measuring the concentration of particulate matter using the tested analysers in parallel with the reference method, SR EN 12341: 2014, and analysis of data series by Pearson correlation and linear regression.

Keywords: accuracy, ambient air, Pearson correlation, PM$_{2.5}$ and PM$_{10}$

Starting from the nowadays pollution reality, when the level of ambient air pollution is at an unprecedented level both in terms of the diversity of the identified pollutants in the air and the increasing concentrations [1-4], continuous and accurate monitoring is an important first step in the process of stopping and improving air quality. In accordance with ISO 5725 standard series - The accuracy (trueness and precision) of measurement methods and measurement results, accuracy reflects the degree of concordance between the result of an attempt and the accepted reference value. The general term of accuracy is used to refer to trueness and precision, at the same time.

Evaluating the trueness of a method involves comparing the value of the acquired results by applying the tested method, which may be a certified reference material (if present) or may be the result of measurement by another method, preferably a reference one. The value of trueness is usually expressed by the trueness error, i.e. the difference between the value obtained by the tested equipment and the value obtained by the reference method. Precision is the general term for the variability of the results of a repeated measurement and is usually expressed based on the values of standard deviations obtained under repeatability/reproducibility conditions with a probability of 95%.

The paper presents the procedure and the results obtained within a project that aimed to establish the accuracy of measurements of PM$_{2.5}$ and PM$_{10}$ made with uRADMonitor A3 a fixed air quality monitoring station (fig. 1a); the trueness and variability were calculated, based on experimental data obtained by parallel measurement of the concentration of PM$_{2.5}$ and PM$_{10}$ using automatic monitors and the reference method, SR EN 12341:2014 and compared with the requirements of acceptability imposed by the regulations under these conditions:

1) the variability condition: to be in line with the uncertainty established by the environmental regulations in force;
2) the Pearson correlation coefficient values, $r \geq 0.97$ according to SR EN 14793: 2017 [5];

Pearson correlation and linear regression methods have been used to verify these requirements, these methods being more and more used in different areas of activity, including environmental protection [6-9].

Experimental part

For the test, PM$_{2.5}$ and PM$_{10}$ particulate matter were determined with two uRADMonitor monitors A and B in parallel with 2 Sven Leckel LVS3 type samplers (Fig.1b), one equipped with PM$_{2.5}$ and the other with PM$_{10}$ impactors according to the reference method for determination of PM$_{2.5}$ and PM$_{10}$ particulate matter concentration in air, SR EN 12341:2014 [10].

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The two monitors uRADMonitor A3 continuously measured and recorded the measurement results at 1 minute for both PM$_{10}$ and PM$_{2.5}$. Determination of particulate matter concentration according to the reference method, SR EN 12341:2014, requires their sampling with dedicated samplers, equipped with impactor heads for separating the two dimensional fractions, PM$_{10}$ and PM$_{2.5}$, on uniquely identified quartz filters, Ø45 mm, conditioned before hand by maintaining in controlled atmosphere at 20°C and 50% humidity, brought to constant and weighed. Exposure is done for a period of 24 hours, followed by conditioning under the same conditions as before sampling, bringing to constant and weighing. The weight gain of filters is the mass of particulate matter retained from the volume of air drawn over a 24-hour period with a flow rate of 2.3m$^3$/h; usually the concentration of particulate matter is expressed in μg/m$^3$.

In order to verify the accuracy of the measurements of the two monitors, the obtained results were analysed by the Pearson statistical correlation method and were compared with the results obtained by the gravimetric reference method. All analyses and statistical tests were performed with SPSS 20.0 program.

Results and discussions

To establish the accuracy of measurements made with uRADMonitor A3 equipment, the trueness and variability were calculated, based on experimental data obtained by parallel measurement of the concentration of PM$_{2.5}$ and PM$_{10}$ using automatic monitors and the reference method [10] and compared with the requirements of acceptability imposed by the regulations under these conditions. Tests ran from Nov 13, 2018 to Dec 11, 2018.

The two Sven Lecke LVS3 samplers, one for PM$_{10}$ and the other for PM$_{2.5}$, were installed on the third floor of the ECOIND building; in the immediate vicinity were mounted both monitors, in a vertical position, on the wall. The results of the measurements, the daily averages, are found in table 1 together with the results obtained by the reference method and the differences between the concentration of reference method and both monitor concentration, μg/m$^3$.

| Period         | PM$_{2.5}$ concentration, μg/m$^3$ | PM$_{10}$ concentration, μg/m$^3$ |
|----------------|-----------------------------------|----------------------------------|
|                | RM      | A   | B   | D$_{A}$ | D$_{B}$ | RM | A | B | D$_{A}$ | D$_{B}$ |
| 13-14.11.2018  | 18.2 | 17.7 | 19.5 | 0.5 | -1.3 | 22.4 | 21 | 23.7 | 1.4 | -1.3 |
| 14-15.11.2018  | 16.7 | 15.5 | 16.3 | 1.2 | 0.4 | 19.5 | 18.4 | 20.1 | 1.1 | -0.6 |
| 15-16.11.2018  | 16.5 | 17.6 | 18 | -1.1 | -1.5 | 21.1 | 20.7 | 22 | 0.4 | -0.9 |
| 16-17.11.2018  | 12.4 | 13.5 | 12.3 | -1.1 | 0.1 | 15.6 | 16.1 | 15.4 | -0.5 | 0.2 |
| 20-21.11.2018  | 18.2 | 16.75 | 17.3 | 1.5 | 0.9 | 19.7 | 19.92 | 21.18 | -0.2 | -1.5 |
| 21-22.11.2018  | 13.1 | 12.3 | 11.97 | 0.8 | 1.1 | 15.0 | 14.81 | 15.22 | 0.2 | -0.2 |
| 22-23.11.2018  | 28.3 | 27.64 | 30.28 | 0.7 | -2.0 | 33.2 | 32.2 | 35.87 | 1.0 | -2.7 |
| 23-24.11.2018  | 25.1 | 24.43 | 26.51 | 0.7 | -1.4 | 29.6 | 28.66 | 31.75 | 0.9 | -2.2 |
| 26-27.11.2018  | 21.7 | 18.94 | 20.04 | -0.2 | -1.3 | 22.7 | 22.35 | 24.3 | 0.3 | -1.6 |
| 27-28.11.2018  | 9.9 | 10.76 | 10.14 | -0.9 | -0.2 | 14.0 | 13.01 | 13.02 | 0.9 | 0.9 |
| 28-29.11.2018  | 8.9 | 9.6 | 8.51 | -0.7 | 0.4 | 12.2 | 11.93 | 11.38 | 0.3 | 0.8 |
| 29-30.11.2018  | 9.6 | 10.5 | 9.45 | -0.9 | 0.2 | 11.9 | 12.88 | 12.38 | -1.0 | -0.5 |
| 3-4.12.2018    | 54.0 | 50.35 | 56.17 | 3.7 | -2.1 | 60.1 | 58 | 65.42 | 2.1 | -5.3 |
| 4-5.12.2018    | 53.2 | 51.57 | 57.25 | 1.6 | -4.1 | 62.3 | 59.33 | 66.41 | 3.0 | -4.1 |
| 5-6.12.2018    | 47.2 | 45.5 | 51.53 | 1.7 | -4.3 | 56.9 | 52.47 | 60.02 | 4.4 | -3.1 |
| 6-7.12.2018    | 31.2 | 31.65 | 33.62 | -0.4 | -2.4 | 39.2 | 36.74 | 39.64 | 2.5 | -0.4 |
| 10-11.12.2018  | 24.8 | 40.02 | 43.77 | 1.3 | -2.5 | 48.2 | 46.28 | 51.16 | 1.9 | -3.0 |
| average        | 24.8 | 24.4 | 26.0 | 0.5 | -1.2 | 29.5 | 28.5 | 31.1 | 1.1 | -1.5 |
| stdev          | 15.27 | 14.33 | 16.69 | 1.29 | 1.62 | 17.14 | 16.25 | 18.92 | 1.36 | 1.72 |
In order to verify the accuracy of the measurements of the two monitors, the obtained results were analyzed by the Pearson statistical correlation method and were compared with the results obtained by the gravimetric reference method.

The results of the statistical correlation analysis (Table 2) show a very good direct correlation between the results with values of the correlation coefficient, $r$, of 0.998 between the PM$_{2.5}$ and the monitor A and of 0.999 for all the other situations.

We can therefore appreciate that the requirement of environmental regulations regarding trueness is ensured for both tested monitors.

**Table 2**

RESULTS OF THE STATISTICAL CORRELATION ANALYSIS BETWEEN THE VALUES OBTAINED FOR PM CONCENTRATION BY THE REFERENCE METHOD AND THE MONITORS A AND B

|          | PM$_{2.5}$ | A$_{2.5}$ | B$_{2.5}$ | PM$_{10}$ | A$_{10}$ | B$_{10}$ |
|----------|-----------|----------|----------|-----------|----------|----------|
| PM$_{2.5}$ | Pearson Correlation | 1        |          |           |          |          |
|          | Sig. (2-tailed)     |          |          |           |          |          |
| A$_{2.5}$ | Pearson Correlation | .998**   | 1        |           |          |          |
|          | Sig. (2-tailed)     | .000     |          |           |          |          |
| B$_{2.5}$ | Pearson Correlation | .999**   | .999**   | 1        |          |          |
|          | Sig. (2-tailed)     | .000     | .000     | .000     |          |          |
| PM$_{10}$ | Pearson Correlation | .997**   | .999**   | .999**   | 1        |          |
|          | Sig. (2-tailed)     | .000     | .000     | .000     | .000     |          |
| A$_{10}$ | Pearson Correlation | .998**   | 1.000**  | .999**   | .999**   | 1        |
|          | Sig. (2-tailed)     | .000     | .000     | .000     | .000     | .000     |
| B$_{10}$ | Pearson Correlation | .999**   | .999**   | 1.000**  | .999**   | .999**   |
|          | Sig. (2-tailed)     | .000     | .000     | .000     | .000     | .000     |

**, Correlation is significant at the 0.01 level (2-tailed).

The same correlation analysis applied to trueness error (D$_A$, D$_B$) between the concentration of particulate matter determined by the reference method and the values indicated by the two monitors, also indicates good and very good correlations between these data series (Table 3).

We can see that in the case of the monitor A, is noted a good direct correlation for PM$_{2.5}$ ($r_{PM2.5} = 0.764$) and a very good direct correlation for PM$_{10}$ ($r_{PM10} = 0.854$), respectively, on the tested concentration range, when the concentration of particulate matter grows, same does the error of trueness. In monitor B, however, we notice exactly the opposite behavior, on the same concentration range; the correlation for the monitor B with the trueness error (D$_A$, D$_B$) is inversely, very good ($r_{PM2.5} = -0.850$; $r_{PM10} = -0.879$), respectively, on the tested concentration range, for the increase of concentration of particulate matter in the air the error of trueness decreases to negative values.

**Table 3**

THE RESULTS OF THE STATISTICAL CORRELATION ANALYSIS BETWEEN THE VALUES OBTAINED FOR THE PM CONCENTRATION BY THE REFERENCE METHOD AND THE TRUENESS ERROR (D$_A$, D$_B$)

|          | PM$_{2.5}$ | DA$_{2.5}$ | DB$_{2.5}$ | PM$_{10}$ | DA$_{10}$ | DB$_{10}$ |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| PM$_{2.5}$ | Pearson Correlation | 1        |          |           |          |          |
|          | Sig. (2-tailed)     |          |          |           |          |          |
| DA$_{2.5}$ | Pearson Correlation | .764**   | 1        |           |          |          |
|          | Sig. (2-tailed)     | .000     |          |           |          |          |
| DB$_{2.5}$ | Pearson Correlation | -.850**  | -.381    | 1        |          |          |
|          | Sig. (2-tailed)     | .000     | .132     | .000     | .000     |          |
| PM$_{10}$ | Pearson Correlation | .997**   | .721**   | -.882**  | 1        |          |
|          | Sig. (2-tailed)     | .000     | .001     | .000     |          |          |
| DA$_{10}$ | Pearson Correlation | .825**   | .547     | -.858**  | .854**   | 1        |
|          | Sig. (2-tailed)     | .000     | .023     | .000     | .000     |          |
| DB$_{10}$ | Pearson Correlation | -.905**  | -.832**  | -.709**  | -.879**  | -.591**  |
|          | Sig. (2-tailed)     | .000     | .000     | .001     | .000     | .012     |

**, Correlation is significant at the 0.01 level (2-tailed); *, Correlation is significant at the 0.05 level (2-tailed).

PM$_{2.5}$; PM$_{10}$ – PM concentrations determined by the reference method; DA$_{2.5}$, DA$_{10}$ – the trueness error between PM concentration by the reference method and by monitor A; DB$_{2.5}$, DB$_{10}$ – the trueness error between PM concentration by the reference method and by monitor B;...
Regarding the variability requirement, to be in line with the uncertainty established by the environmental regulations in force [11] for this test, namely 25% of the Limit Value (VL) established by Law 104/2011 [12]; according to this regulation VL for PM$_{10}$ is 50μg/m$^3$ for daily average. For PM$_{2.5}$, European regulations do not establish VL for daily averaging; in these conditions, for examination we used a daily VL of 35μg/m$^3$ established by US EPA.

The results of these tests are found in Table 4 where $D_A$, $D_B$ is the trueness error between the particulate matter (PM) concentration determined by the reference method and the results indicated by the A, B monitor, $U_{rel}$ is the relative uncertainty, % of VLE, $U_{abs}$ is the absolute uncertainty, μg / m$^3$ and $I_{max}D_I$ is the modulus of maximum value of the trueness error. It can be seen that both conditions are satisfied both by monitor A and monitor B:

1) the modulus of the maximum values of the trueness errors are less than the absolute uncertainty value for $k = 2$ ($U_{abs}$, μg/m$^3$) of 8.75 μg/m$^3$ value for PM$_{2.5}$ and 12.5 μg/m$^3$ value for PM$_{10}$;

2) the correlation coefficient values are greater than 0.97, respectively $r = 0.99$ for both monitors and dimensional fractions of PM.

### Table 4
THE ACCEPTANCE TEST RESULTS FOR ACCURACY

| Parameter | PM$_{2.5}$, μg/m$^3$ | PM$_{10}$, μg/m$^3$ |
|-----------|----------------------|----------------------|
|           | $D_A$                | $D_B$                |
| minimum   | -1.1                 | -4.3                 |
| maximum   | 3.7                  | 1.1                  |
| Limit value, μg/m$^3$ | 35       | 50                   |
| $U_{rel}$, % from VL | ±25 for $k=2$ | ±25 for $k=2$ |
| $U_{abs}$, μg/m$^3$ | ±8.75 for $k=2$ | ±12.5 for $k=2$ |
| $I_{max}D_I$ | 3.7 < 8.75 for $k=2$ | 4.3 < 8.75 for $k=2$ |
| correlation coeff., $r$ | 0.998 | 0.999 |

Starting from the very good correlation between the PM concentration values determined by the reference method and the values indicated by the two uRADMonitor A3 monitors correction relations were obtained by the linear regression method. The results of the analysis and correction equations of the form $Y = C_1 x + C_0$ are presented in table 5, where $Y$ represents the corrected values of the monitors indications, $x$, and $C_0$, $C_1$ represents the regression coefficients, respectively the ordinate at origin ($C_0$) and the slope of the regression curve ($C_1$).

### Table 5
THE RESULTS OF LINEAR REGRESSION ANALYSIS FOR: a) PM$_{2.5}$ MEASURED WITH MONITOR A; b) PM$_{2.5}$ MEASURED WITH MONITOR B; c) PM$_{10}$ MEASURED WITH MONITOR A; d) PM$_{10}$ MEASURED WITH MONITOR B

| Coefficients* | Model | Unstd. Coeff. | Std. Coeff. | t | Sig. |
|---------------|-------|---------------|-------------|---|------|
| (Constant)    | B     | Std. Error    | Beta        |   |      |
| A2.5          | -1.110| .448          | -2.475      | .026|
| B2.5          | 1.065 | .016          | .998        | 66.665 | .000 |
| a. Dependent Variable: PM$_{2.5}$ |
| $Y_{PM_{2.5-A}} = 1.065 x PM_{2.5-A} – 1.110$ |

(a)

| Coefficients* | Model | Unstd. Coeff. | Std. Coeff. | t | Sig. |
|---------------|-------|---------------|-------------|---|------|
| (Constant)    | B     | Std. Error    | Beta        |   |      |
| B2.5          | 1.031 | .371          | 2.775       | .014 |
| a. Dependent Variable: PM$_{2.5}$ |
| $Y_{PM_{2.5-B}} = 0.915 x PM_{2.5-B} + 1.031$ |

(b)

| Coefficients* | Model | Unstd. Coeff. | Std. Coeff. | t | Sig. |
|---------------|-------|---------------|-------------|---|------|
| (Constant)    | B     | Std. Error    | Beta        |   |      |
| A10           | -0.863| .395          | -2.187      | .045 |
| a. Dependent Variable: PM$_{10}$ |
| $Y_{PM_{10-A}} = 1.069 x PM_{10-A} – 0.863$ |

(c)

| Coefficients* | Model | Unstd. Coeff. | Std. Coeff. | t | Sig. |
|---------------|-------|---------------|-------------|---|------|
| (Constant)    | B     | Std. Error    | Beta        |   |      |
| | 1.069 | .012          | 88.292      | .000 |

| Coefficients* | Model | Unstd. Coeff. | Std. Coeff. | t | Sig. |
|---------------|-------|---------------|-------------|---|------|
| (Constant)    | B     | Std. Error    | Beta        |   |      |
| | 1.069 | .012          | 88.292      | .000 |

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By using these correction relations, in the case where reporting the accuracy is not required, the corrected value can be calculated in relation to the reference method. In the previous example for a monitor A indication of 16.7 μg/m³ PM₁₀, the corrected value is 16.98 μg/m³ calculated with the relation from table 5-2c.

Conclusions

Based on the conducted tests and the obtained results, we can assume that the two uRADMonitor A3 monitors produced by SC MAGNASCI SRL Timisoara, subjected to tests for accuracy measurements evaluation, can be used for the continuous monitoring of the PM₂.₅ and PM₁₀ in the air, their performances aiming at measuring accuracy, fit in acceptability conditions:

1) meets the variability condition: it falls within the uncertainty established by the environmental regulations in force, below 25% of the Limit Value (VL) for PM₁₀ of 50μg/m³ for daily averaging and, 25% of the Limit Value (VL) for PM₂.₅ of 35μg/m³ according to US EPA.

2) the correlation coefficient between the A and B monitor indications and the obtained value using the reference method \( r \geq 0.97 \), respectively \( r = 0.99 \) for both monitors and dimensional fractions of particulate matter.

Considering the good and very good correlation between the particulate matter concentration values indicated by the two monitors and by the reference method, correction relations were obtained by the linear regression method with which we can calculate the corrected value \( Y_{PM} \) in relation to the reference method by the monitor value indicated \( X_{PM} \).

For automated monitoring systems, as is the case of uRADMonitor A3 monitors, these correction relations can be included in the software’s equipment, the monitors indicate the corrected values and the trueness error is compensated in this case.

We mention that these relations are applicable only on the tested concentration ranges with an extrapolation of maximum 10%; domain limits are given by the minim, respectively maxim in table 1, for each dimensional fraction of particulate matter and monitor.

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