HOW TO EFFECTIVELY ANALYSE THE IMPACT OF AIR QUALITY ON SOCIETY – REVIEW OF MODERN MEASUREMENT TECHNIQUES AND APPARATUS: PARTICULATES

Abstract

The article discusses modern measurement techniques and equipment designed for air quality analysis. The problem of the quality of atmospheric and indoor air is strongly related to broadly understood public health. Modern measurement techniques allow faster and more effective assessments of the air quality condition in a given place. The paper discusses the structure, measurement method of solid pollutants and automatic measurement systems deploying the micro-oscillatory balance method, using the interaction of ionizing radiation with matter-suppression of beta radiation and gamma radiation spectrometry, optical methods based on light scattering on particles of particular matter and systems combining more than one method. Technical solutions introduced by manufacturers of measuring equipment, which allow more precise measurement of gaseous pollutants, were also discussed.

Keywords: Particular matter, PM10, PM2.5, XRF spectrometry, PM concentration, elemental composition, PM automatic measurement.
JAK SKUTECZNIE ANALIZOWAĆ WPŁYW JAKOŚCI POWIETRZA NA SPOŁECZEŃSTWO – PRZEGLĄD NOWOCZESNYCH TECHNIK I APARATURY POMIAROWEJ

Abstrakt

W artykule omówiono nowoczesne techniki pomiarowe i urządzeń do analizy jakości powietrza. Problem jakości powietrza atmosferycznego i wewnętrznego jest silnie związany z szeroko rozumianym zdrowiem publicznym. Nowoczesne techniki pomiarowe pozwalają na szybszą i skuteczniejszą ocenę stanu jakości powietrza w danym miejscu. W artykule omówiono budowę, metodę pomiaru zanieczyszczeń stałych oraz automatyczne systemy pomiarowe wykorzystujące metodę wagi mikrosilownikowej, wykorzystujące oddziaływanie promieniowania jonizującego z materią - tłumienie promieniowania beta i spektrometrię promieniowania gamma, metody optyczne oparte na rozpraszaniu światła na poszczególnych cząstkach materii oraz systemy łączące więcej niż jedną metodę. Omówiono również rozwiązania techniczne wprowadzone przez producentów sprzętu pomiarowego, które pozwalają na bardziej precyzyjny pomiar zanieczyszczeń gazowych.

Słowa kluczowe: Materia szczegółowa, PM10, PM2,5, spektrometria XRF, stężenie PM, skład pierwiastkowy, pomiar automatyczny PM.

1. Introduction

The problem of air quality is the subject of a wide social debate; however, effective environmental management requires the development and validation of new measurement techniques. Nowadays, when information is of great value and can contribute to a quick change of reality, reliable measurements and the speed of their acquisition are the key parameters. The public should have access to air quality data as part of environmental justice, and they must be informed quickly in the event of deterioration, in their quality of life, or a threat to their health. Previous measuring techniques are not always able to meet these requirements. This raises the need for measurement techniques that are able to provide the same air quality information faster, more accurately, or with less effort or resources. Thanks to this, it is possible to carry out measurements in real-time [1], and by connecting them with spatial information systems, make them available to the public [2], [3], and take into account new parameters in the assessment of social exposure [4], [5]. Thanks to new measurement techniques, public awareness about the dangers of air pollution is growing. Among other things, it is the data on air quality collected with the use of modern techniques, by enthusiasts and social activists, which can be the basis for new legal regulations [6]. The role of the R&D (research and development) sector is to ensure the accuracy of the information available to the public, i.a. by validating these techniques [7] and creating new ones. In this article, modern techniques for measuring solid pollutants will be discussed in the context of the current standards, along with the application of devices that use these techniques.
2. Measurement techniques and apparatus

2.1. Measurement of solid pollutants

2.1.1. PN-EN 12341:2014 Standard gravimetric measurement method for the determination of the PM10 or PM2.5 mass concentration of suspended particulate matter

First of all, let us quote a fragment of the PN-EN 12341: 2014 (PN-EN 12341: 2014) [8] standard that describes the gravimetric measurement method for the determination of mass concentrations of suspended particulate matter:

“In order for air quality throughout the European Union to be assessed in a consistent manner, Member States must use standard techniques and measurement procedures. The purpose of this European Standard is to provide a harmonized methodology for measuring the mass concentrations of particulate matter (PM10 and PM2.5 respectively) in the ambient air, in accordance with Directive 2008/50/EC on ambient air quality and cleaner air for Europe, which specifies parameters specific to assessment of the concentration levels of particulate matter in the air.”

Particular matter collection is carried out by taking a PM sample onto the filter and then weighing it on a filter equipped with a scale. The sampling itself is performed using the so-called PM collectors (or sequential PM collectors), furnished with a standardized inlet, i.e., a measuring head, the design of which is described in the above-mentioned standard. The PM collector works with a nominal flow rate of 2.3 m$^3$/h. This intensity is most often controlled with the help of built-in mass flow meters. The nominal sampling period is 24 hours (24-hour averages). Measurement results are expressed in µg/m$^3$, where the air volume corresponds to the volume at ambient conditions, near the inlet, at the time of sampling. Thanks to the changer and cassette with a minimum of 14 filters, the sequential PM collector allows the sampling for at least 2 weeks, without the need of replacing filters by the operator. However, the application of such a solution requires proper conditioning of the filters, which after 24 hours of exposure to the sample are found in a cassette with once-collected PM in a cassette, waiting to be taken for further analysis by the operator.

2.1.2. PN-EN 16450:2017 Automated measuring systems for the measurement of the concentration of particulate matter (PM10; PM2.5)

Moving on to the next standard, it is applicable to automatic measurement systems for suspended PM concentration; let us quote a fragment of the introduction to the standard (PN-EN 16450:2017) [9]: In order to comply with the requirements of the EU Air Quality Directive, the reference methods given in Directive 2008/50/EC for the measurement of particulate matter mass concentration are not widely used in automatic air pollution monitoring networks. Typically, these networks
use automated continuous measurement systems (AMS), e.g. based on the use of an oscillating microbalance, β-radiation absorption, or in situ optical methods. Such AMS systems are usually able to obtain 24-hour average measured values with a measurement range of up to 1,000 µg/m³ and 1-hour average measured values up to 10,000 µg/m³, if applicable, where air volume is the volume in ambient conditions near the inlet.

The PN-EN16450: 2017 standard does not define a specific measurement methodology to be used for the automatic determination of mass concentration of solid particles in atmospheric air; therefore, various measurement methods can be used. Nevertheless, the measuring instrument should consist of:

- PM10 or PM2.5 selective measuring head. This head is used to selectively separate the PM fractions of interest from the total PM (in the case of optical analysers, such heads are not used, and a separation system is required instead);
- Sampling system/tube. Such an arrangement is usually of a length that corresponds to certain conditions regarding the height, from which the sample is to be taken. Most often it is equipped with “intelligent heating” depending on the external temperature and humidity. This heating is intended to eliminate the effect of volatile fractions released from the measuring filter. Another possible solution is a system of partial drying of the air sample;
- A vacuum pump responsible for sample collection;
- Flow sensors and controllers;
- Temperature and pressure sensors;
- Data recording system-logger: hardware and software for collecting and storing data and converting measurement results.

In addition, the automatic analyser for measuring solid particles can be equipped with moisture sensors or a compensation measurement system. Such a system is used to eliminate the influence of undesirable confounding factors or accidental changes in the determination of the mass of particulate matter.

Automatic devices for measuring particulate matter approved for operation in air pollution monitoring networks should obtain a certificate and a Type Approval report for compliance with the PN-EN 16450: 2017 standard. Such tests and the report must be issued by an accredited laboratory, i.e. a laboratory with accreditation to the EN ISO / IEC 17025 standard for the tests performed. The methodology for the procedure, for confirming equivalence, must be in accordance with EN 16450: 2017.
2.2. The method of oscillating microbalance

This methodology was invented in the 1990s by two Americans, Rupprecht and Patashnick [10]. This discovery resulted in the founding of a company that produces a number of instruments using the oscillating balance method.

The most popular representative of instruments using the oscillating microbalance method is the Teom 1400 series of PM meters (Thermo Fischer Scientific, Walthman, MA, USA), represented by: Teom 1400, Teom 1400a, Teom 1400ab, and Teom1405. The principles of mass measurement used by Teom instruments differ fundamentally from those on which most other measuring instruments have been based. The filter is mounted on a capillary, the so-called conical element (a thin, long, hollow glass tube). A capillary filter is placed in the sample flowing stream. The “fall” of individual PM particles onto the filter causes the capillary to vibrate. The conical element vibrates exactly at the natural frequency. The effect is similar to the vibration of a tuning fork. As the mass increases, the frequency of vibrations tends to decrease. The electronic control circuit senses these vibrations and, through positive feedback, adds sufficient energy to cover system losses. The automatic gain control circuit maintains a constant vibration amplitude. An accurate electronic counter measures the frequency in two-second sampling periods. The dependence of the frequency changes on the change of the mass of the vibrating element makes it possible to determine the mass gain over time [10].

Fig. 1. Filter with a conical element induced to vibrations due to contact PM (3)
The principle of mass measurement is described by the formula (1), where  \( \Delta M \) is the mass change,  \( K_0 \) is the capillary stiffness (taking into account the mass conversion),  \( f_0 \) – the initial frequency and  \( f_1 \) – the final frequency [10].

\[
\Delta M = K_0 \left( \frac{1}{f_1^2} - \frac{1}{f_0^2} \right)
\]  

(1)

At the beginning of the 21st century, the so-called “effect of loss of volatile fractions” was worked out, which introduced a large error in the measurement of the oscillatory microbalance method, which means that this method is susceptible to the above-mentioned problem. The essence of the “volatile fraction loss effect” is the deposition of PM, including volatile fractions, on the measuring filter, which
causes vibrations. With time, volatile particles deposited on the filter will once again transform into a volatile form, which disturbs the actual vibration value. To eliminate the above-mentioned effect, an additional component installed in the sampling path was constructed, called FDMS (Filter Dynamics Measurement System). This system divides the measuring cycle into two stages of 6 minutes each. In the first stage, the sample flows through the instrument along the “old path” and is deposited on the measuring filter. In the second stage, the sample additionally flows through the FDMS system, where it is heated to evaporate volatile fractions. Thanks to this, the device not only eliminates the evaporative effect of volatile fractions but also has the ability to measure the mass of solid particles, with the separation into volatile and non-volatile fractions. This device is widely used in air quality monitoring [11] and in connection with other parameters of the atmosphere quality [12].

Fig. 4. Scheme of Teom 1400ab FDMS: a – measuring head PM10, b – FDMS (Filter Dynamics Measurement System), c – module SES, d – control unit, e – measurement unit, 1 – main flow, 2 – pump, 3 – by-pass flow, 4 – by-pass flow, 5 – baseline/reference flow, 6 – baseline/reference flow, 7 – rinsing flow (3)
One of the interesting facts about automatic measurement systems is that when, at the turn of the 20th and 21st centuries, the European Union started to devise a standard describing automatic PM measurement, the concept of describing the oscillatory microbalance method as the required measurement method has won. As Rupprecht & Patashnick (the company was founded to commercialize the invention) patented its method, negotiations with the manufacturer began. The EU imposed a condition that the patent would be made available free of charge to all interested parties. After long negotiations, the agreement has not been concluded, and we had to wait until 2017 for the standard describing automatic measurement systems, for measuring the concentration of particulate matter.

### 2.3. β radiation suppression method

The β-radiation absorption method is known and very well-tested. A number of measuring instruments make use of this method to measure the concentration of PM in the atmospheric air [13].

It is known that high-energy electrons from the radioactive decay of carbon $^{14}$C react with nearby molecules, as a rule losing their energy. Sometimes they are also absorbed by it. These electrons are called β rays, and the process that takes place is called β radiation suppression [14].

Let us imagine a system, in which between the source of radioactive carbon $^{14}$C and the β-ray detector a material is placed (e.g. a filter tape), on which a sample of solid particles is then deposited. This sample would absorb the beta rays emitted by the source and their energy would be reduced. As a result, the detector receives less β radiation than has been emitted by the source.

The difference between what has been emitted and what has been measured by the detector (and thus the degree of particle number reduction) is a function of the mass, of the absorbing material in the path of the beta rays.

![Fig. 5. Example of the construction of a PM meter using the β-radiation attenuation method (3)](image)
The number of $\beta$ rays passing through the absorbing material decreases exponentially with the mass of the material, through which they pass according to equation (2), where $I$ is the measured radiation $\beta$ intensity, $I_0$ the measured intensity of undamped beta radiation (measurement made on a clean measuring tape), $\mu$ cross-section of beta-ray absorbing material (cm$^2$/g), $x$ the density of the absorbing substance (g/cm$^2$) [14].

$$I = I_0e^{-\mu x}$$

(2)

This equation is very similar to those describing the attenuation of gamma particles, however, in the case of gamma radiation, the radiation spectrum is continuous and the rate of loss of free electrons is higher than the faster electrons, which causes deviations from the linear dependence in the exponent. Equation (2) is an idealizing simplification of the actual process to simplify the related mathematical apparatus. Nevertheless, the manufacturers’ research has shown that in properly designed devices deploying $\beta$ radiation suppression, the use of the above-described formula does not cause the appearance of significant differences.

2.4. Optical method

In recent years, optical methods have been gaining more and more importance, both in simple applications (simple, cheap, installed in hundreds of pieces, measuring systems informing more about the level of contamination - so-called indicators) and in “reference” applications, i.e., instruments fully certified for compliance with the applicable EN 16450:2017 standard.

There are several varieties of optical methods used in the measurement of PM, the most popular of which are nephelometry and spectrometry.

![Diagram of an optical spectrometer system](image)
In general, the main principle of all optical instruments is the diffusion of light onto solid particles. In the case of nephelometry, the detector placed most often at an angle of 90° from the light source, which may be, for example, a LED diode, laser, etc., measures the intensity of light reflected from solid particles.

In the case of spectrometry, it is more complicated, yet the measurement is much more accurate. Spectrometers count particles and determine the particle size for each, individual molecule using scattered light, e.g., according to the Lorenz-Mie law. The source of light (usually polychromatic) is a laser or LED diode. Scattered light reflected from the particle passes through the laser beam and is then reflected by the mirror at an angle of 90° to the detector. The determination of the optical particle size is performed by assigning the scattered light signal to the particle diameter with a calibration curve. The use of a polychromatic light source makes it possible to obtain an accurate calibration curve, without ambiguities in the Mie range. This enables a high resolution of the method to be obtained.

Fig. 7. Example of a calibration curve for the detection of 90° scattered light with a monochromatic light source (left) and a polychromatic light source (right)(1)

Fig. 8. An example of a Fidas200 optical aerosol spectrometer (1)

The main advantage of optical analysers - spectrometers is the identification of fractions for each molecule. As a result, it is possible to simultaneously measure many PM fractions with a single measuring instrument. No other methodology for measuring solid particles offers such a possibility. Another important advantage
is the practical lack of consumables, such as filters or measuring tapes (which significantly reduces operating costs).

In recent years, optical instruments (not only reference ones) have gained enormous popularity. Due to the fact that several fractions are measured simultaneously, especially PM10 and PM2.5, these instruments dominate the atmospheric pollution monitoring networks, both domestic (in Poland: the SEM network belonging to the Chief Inspectorate of Environmental Protection CIEP, and managed by the Central Research Laboratory CRL) and local ones (e.g. city, company, etc.).

The main advantage of measuring several fractions with a single instrument is that it eliminates “electronic noise” emitted by the instruments. Each analyser emits a noise on a different level. For example: when measuring PM10 and PM2.5 fractions with the use of two independent analysers, an effect was observed at very low concentrations when the analyser concentration of PM10 fraction (this fraction includes the PM2.5 fraction) measured at lower concentrations of particulate matter than the analyser measuring the PM2.5 fraction. An example of such an effect is a higher indication of PM2.5 than PM10 (which happens relatively often), measured at a single measuring point by two different instruments. By using one device, the above problem is eliminated. Another aspect is the purchase and operating costs, which are lower for one instrument measuring several fractions than for a bank of analysers measuring one fraction each. Another advantage are smaller dimensions and one sampling system, which facilitates the preparation of the measuring point, but also enables comprehensive measurement of many fractions in places inaccessible to single-fraction instruments. This method allowed a more precise analysis of the distribution of the number of particles as a function of diameter, in order to more precisely compare different measurement points [15], and to analyse these distributions in places where the emission from wood combustion is dominant [16].

### 2.5. Other measurement methods

In addition to the basic (most commonly used) measurement methodologies described in the EN 16450: 2017 standard used in instruments for particulate matter, there are additional instruments that use at least two methods simultaneously, so-called hybrid devices.

An example of such a solution is the device called the Synchronized Hybrid Ambient Realtime Particulate Monitor SHARP 5030, of one of the most renowned manufacturers, combining the optical nephelometry method with the β radiation absorption method. The advantage of the nephelometer is the short measurement time, while its disadvantage is the accuracy of the measurement. The opposite is the
case with the beta radiation suppression method, where we obtain high accuracy, but unfortunately, the shortest measurement time is 1h. Thanks to the use of both methods in parallel (the nephelometer carries out the measurement and is permanently and automatically calibrated with the β radiation suppression system), the device benefits from the advantages of each method (and also eliminates their disadvantages) and is able to make measurements very precisely, providing at the same time one-minute results, while ensuring a high detection threshold. It was used inter alia for the analysis of PM2.5 sources during the episodes of atmospheric turbidity [17] and for the analysis of aerosol formation [18].

Another interesting instrument is the ELPI+ (Electrical Low Pressure Impactor). The analysed gas, which contains PM, passes through a device that gives the particles an electric charge in the process of a corona discharge. Then the sample containing the charged PM particles is placed in a multi-stage impactor, the stages of which are electrically isolated from each other. PM with a decreasing aerodynamic diameter from 10 μm to 0.006 μm are deposited on the individual stages (14 elements) of the impactor. When a particle falls on the impactor stage, the charge of the PM particle is collected on the impactor stage. The charge is measured in real-time by a highly sensitive multi-channel electrometer. The electrical signal from each of the impactor stages is converted into data on the distribution of the number and mass of particles according to their size, i.e. the aerodynamic diameter. An additional advantage of this solution is the collection of individual PM fractions on measuring filters. The collected sample can be used not only to confirm (using gravimetric methods) the correctness of the automatic measurement indication but also for further laboratory analyses. In such a way, we can obtain information, for example, on the elemental composition of the collected sample [19].
Thanks to its real-time measurement, ELPI+ is an ideal tool for PM analyses in conditions of unstable concentrations and variable fractional distribution. A durable and solid construction allows the device to be used also in difficult environmental conditions; it was used inter alia in determining the parameters of emissions from low-emission coal power plants [20], aerosol analysis in dental offices in the context of SARS-CoV-2 virus transmission [21] or in the analysis of emissions from waste fires [22]. The latest versions of the above solution, although a bit simplified, and consequently also miniaturized, provide a wide range of possibilities for its use in measuring air pollution in buildings [23]. The aspect of air pollution we breathe in buildings (homes, shops, offices, etc.) is becoming increasingly important, especially since indoor time has drastically increased in recent decades. Miniaturization also allows the use of these devices in mobile air quality monitoring [24].

Another device, an even more interesting one, is the Horiba PX-375 analyser. This instrument combines β radiation absorption with XRF spectrometry. Thanks to the innovative combination of these two measurement methodologies, the manufacturer has gained the unique possibility of automatic, practically in real-time, measurement of the concentration of PM10 or PM2.5 solid particles, with the simultaneous spectral analysis, thanks to which the user obtains information about the elemental composition of the measured PM.

There is a need for simultaneous measurement of PM and its chemical properties in order to quickly adjust process parameters and identify emission sources. This proves to be particularly useful in areas where PM emissions from different sources overlap or where there is only one dominant source and the problem is to correctly identify the origin of the PM. The use of the PX-375 analyser in the research enables the acquisition and use of data (PM concentration, but most of all the exact elemental composition of the tested PM) from averaging measurements at time intervals shorter than 24 hours. The use of traditional measurement methodologies excludes capturing short-term elevated concentrations of elements in the atmosphere. Long-term measurement allows both the definition of short-term changes and
the characteristics of pollutants at the regional level, as well as the use of recorded concentrations of inorganic elements as indicators in the identification of pollution sources [25], [26], a comparison of actual concentrations with environmental indicators [27], even if it is known that in rural ones, low emission can significantly worsen air quality. Hence, cheap and easily accessible methods of monitoring are needed. Recently, spider webs biomonitoring is getting popular, however, there is no information about its comparison with active methods. In this study, PTEs accumulated on spider webs were compared with results from continuous particulate monitor (CPM and environment monitoring [28], [29].

3. Conclusions

The apparatus is a key element in air quality measurements. The measurement of solid pollutants can be performed by various technical solutions, which should be compliant with standards for automatic measurement systems. Equipment manufacturers are devising modern solutions and techniques aimed at providing society with better access to more reliable data on air quality. It is important that the recipients of information on airborne pollutants be aware of the various methods of measuring parameters, and hence the differences between them and the advantages of individual methods. Due to the flexibility presented in the EN 16450 standard, the methods used in various devices differ from each other.

The measuring instruments described in this publication and the methodologies they use can be deployed successfully in diverse applications.

Manual methodologies (gravimetric samplers) are applicable when measurements should meet the requirements described in the European Union regula-
tions, i.e., for example all official settlements of the PM concentration occurring in the atmospheric air. Due to the long analysis time manual methodologies are unsuitable for hot-spot measurements, where results are expected immediately or almost immediately.

If, in addition to the concentration of PM, we are also interested in the separation of volatile and non-volatile fractions, the only possible solution are instruments that use the oscillatory microbalance method together with the FDMS system.

Optical methods are ideal for hot-spot, fast, short-term measurement applications. However, for example, to detect the sources of PM emissions, an excellent solution is to measure its elementary composition of PM are XRF methodologies.

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References

How to effectively analyse the impact of air quality on society...


