

Vzroki nezanesljivosti vzorčnih meritev pri določevanju koncentracije delcev v plinastem okolju

Causes of Sampling Measurement Uncertainties when Determining the Particle Concentration in a Gaseous Environment

Nastia Degiuli¹ - Nikola Barbalić² - Goran Marijan²

(¹University of Zagreb, Croatia; ²Hrvatska elektroprivreda Zagreb, Croatia)

Merjenje koncentracij delcev je pomembno za veliko področij uporabe. Tako je predvsem od šestdesetih let prejšnjega stoletja, ko je bilo dokazan njihov škodljiv vpliv na zdravje ljudi. Pri merjenju koncentracij delcev pride do precej večjih napak, kakor pri merjenju emisij in/ali imisij drugih onesnaževal na področju ohranjanja kakovosti zraka. Pregledovanje posebnosti delcev v skupini onesnaževal zraka ter priprava splošnih standardnih oznak za emisijske in/ali imisijske količine za primer delcev zahtevata uporabo ene od dveh nasprotujočih si in skrajnih poenostavitev: sistem plin-delci obravnavamo v razmerah kontinuiranega okolja ali kot niz diskretnih trajektorij delcev v plinu. Zaradi omejitev razpoložljivih merilnih postopkov je rezultat v obeh primerih prikaz srednje vrednosti jakosti masnega toka, kot zmnožek srednje hitrosti in srednje vrednosti koncentracij, ki že v naprej vsebuje merilno napako. V tem prispevku smo se osredotočili na vzorčne lastnosti med določevanjem koncentracije delcev, ki so glavni vir merilne nezanesljivosti, ter na omejitve njihove izločitve v praksi.

© 2007 Strojniški vestnik. Vse pravice pridržane.

(Ključne besede: koncentracija delcev, merilne negotovosti, vzorčenje, pogreški)

Measuring particle concentrations is very important in many applications; this has been particularly so since the 1960s, when their harmful influence on human health was proved. Measuring particle concentrations has a much greater measurement error than when measuring the emissions and/or immissions of other pollutants in the field of air-quality protection. Viewing the peculiarities of particles within the group of air pollutants, the elaboration of general standard specifications for emissions and/or immission quantities in the case of particles requires an approach to one of the two contradictory and extreme simplifications: the gas-particle system is either viewed in terms of a continuous environment or as a set of discrete particle trajectories in a gas. Due to the limitations of the available measurement procedures the result in both cases is the presentation of the mean value of the mass flow density as a product of velocity and concentration mean values, implying in advance a measurement error. In this paper attention has been focused on the sampling characteristics during the determination of the particle concentration, which are the main sources of measurement uncertainty, and on the limitations of their elimination in practice.

© 2007 Journal of Mechanical Engineering. All rights reserved.

(Keywords: particles concentration, measurement uncertainties, sampling, measurement errors)

0 INTRODUCTION

An investigation of the state and/or the motion of a discrete, dispersed particle system in a fluid environment is of great importance for scientific and professional developments in many areas of human

activities: the power industry, processing techniques, agriculture, meteorology, protection of the environment, health services, etc. For example, fluid flows and their dispersed particles (solid particles, droplets, bubbles) are the working body in various types of equipment with technical applications. In

such cases, the behaviour of the dispersed phase directly determines the equipment's operational characteristics, and for this reason particle trajectories represent an important step in the investigation of their function and are a basis for the development of their designs. Moreover, the problem of air pollution caused by flowing particles has been given increasing importance since it has been proved that their concentration in the air is one of the components that determines the level of their harmful influence on health. Other important components of health risks are the proportions in particular fractions according to particle size, chemical composition, mixtures, corrosiveness, radioactivity, fusibility, roughness, etc. Because of this, measurement procedures for the determination of the properties of different flowing particles are more demanding and are subject to a greater measurement uncertainty than the measurement procedures for the determination of the properties of other air pollutants. For every investigation of particles it is necessary to ensure a representative material sample. Exceptions are particular optical procedures that are preceded by a calibration with a material particle sample. Sampling is almost always a major source of measurement uncertainty when determining the particle state and/or the properties in a particle-fluid discrete, dispersed system. For such a system the sampling is realized by the suction of a limited volume (sample) of the particle-fluid dispersed system through a corresponding suction opening. The basic requirement is the sample's representative quality, i.e., its (sufficiently approximate) identity with the authentic dispersed system, with regard to the quantity that is established (concentration, particle size distribution, chemical composition, etc.). The question of representative quality should be dealt with during every sampling procedure.

Changes in the characteristics of the particle-fluid dispersed system sample, especially its concentration and particle size spectrum, can occur at the spot where the sample was taken, i.e., before being taken into the measurement device, as well as on the path through the suction pipe and through other components of the device, and finally, during further handling actions to the place where the desired analysis is performed. In this way, smaller or greater differences between the measured and the real quantities that are measured occur, resulting in corresponding measurement errors that belong to the group of systematic errors. Attention will be di-

rected to the part of the errors that occur during the sampling of the particle-fluid dispersed system to the point where the sample is taken into the suction opening of the measurement equipment. As opposed to gas mixtures, for which the representative sample is relatively simply achieved, the representative sample of particle-fluid, and especially particle-gas, dispersed system is always questionable and requires additional verification.

1 DEFINITIONS OF EMISSION AND IMMISSION QUANTITIES

According to HRN ISO – Vocabulary [1], emission and emission quantities are expressed as follows:

D.1. Emission: Discharge of substances into the atmosphere. The point or the area from which the discharge takes place is called the source. The term is used to describe the discharge and the rate of discharge. The term can also be applied to noise, heat, etc.

D.2. Emission rate (emission velocity): The mass (or any other physical quality) of pollutant emitted into the air per unit of time.

D.3. Emission rate density (emission flux): Emission flux divided by the area of a corresponding emission source.

Immission and immission quantities have the same meaning as emission and emission quantities, but with the opposite sign. Simply, the receptor substitutes the source, and all the rates/transitions are in the direction from the air to a particular receptor instead of in the direction from a source into the air. Thus, the HRN ISO Vocabulary [1] confirms: "immission....is the opposite of emission". A mathematical determination of the terms *immission* and *emission* is given in ISO/TR 4227 [2] in terms of immission and emission flow, but unfortunately, with some omissions and errors [3]. Taking into consideration the discussion in paper [3], the immission/emission flow terms, in relation to ISO/TR 4227 [2], could be correctly defined in the following manner:

D.4. Immission rate $I(t)$ to a particular receptor is defined by the enveloping surface integral:

$$I(t) = \int_{F_i} \rho \cdot (\vec{v} \cdot \vec{n}) \cdot dF_i \quad (1)$$

D.5. Emission rate $E(t)$ of a source is defined by the enveloping surface integral:

$$E(t) = \int_{F_e} \rho \cdot (\vec{v} \cdot \vec{n}) \cdot dF_e \quad (2)$$

where (in two preceding equations):

$F_{\parallel}|F_E$ – is the smallest enveloping surface around the receptor|source,

ρ – is the density (a property divided by volume) at the enveloping surface $F_{\parallel}|F_E$,

\vec{v} – is the velocity vector of the property at the enveloping surface $F_{\parallel}|F_E$,

\vec{n} – is the normal vector of the enveloping surface element $dF_{\parallel}|dF_E$ pointing outwards so that the following is valid:

$$\int_{F_i} (\vec{v} \cdot \vec{n}) dF_i \geq 0, \quad \int_{F_E} (\vec{v} \cdot \vec{n}) dF_E \geq 0 \quad (3),$$

$\rho \cdot \vec{v}$ – is the immission|emission flux/rate density on the enveloping surface $F_{\parallel}|F_E$.

The definition of Equation (1)|(2) for the immission|emission rate cannot be strictly applied to solid or liquid particles because of their discrete distribution. Here, the quantity ρ – property (for particles it is usually the mass m) divided by volume, might be considered in the following two ways:

(i) The elementary volume ΔV in the vicinity of each observed point $P(\vec{r})$ in space is sufficiently large at a given moment of time and it still contains a large number of particles, which makes it representative for describing the spatial distribution of particles. Thus:

$$\rho = \frac{\Delta m_p}{\Delta V} = c_m(\vec{r}, t) \quad (4),$$

represents the particle mass concentration field that, from the said condition, is continuous at all points on the surface $F_{\parallel}|F_E$ so the immission|emission rate according to Equation (1)|(2) is equal to:

$$I(t)|E(t) = \dot{m}_p(t) = \int_{F_i|F_E} c_m(\vec{r}, t) \cdot \vec{v}_p(\vec{r}, t) \cdot \vec{n}(\vec{r}) dF = [c_m(t) \cdot \vec{v}_p(t)] \cdot F \neq \overline{c_m(t)} \cdot \overline{\vec{v}_p(t)} \cdot F \quad (5),$$

where for average values $\overline{c_m(t)}$ and $\overline{\vec{v}_p(t)}$ over the surface $F_{\parallel}|F_E$ the following applies:

$$\overline{c_m(t)} = \frac{1}{F} \int_{F_i|F_E} c(\vec{r}, t) dF \quad (6),$$

$$\overline{\vec{v}_p(t)} = \frac{1}{F} \int_{F_i|F_E} [\vec{v}_p(\vec{r}, t) \cdot \vec{n}(\vec{r})] dF$$

where $F = F_{\parallel}|F_E$.

(ii) The elementary volume ΔV in the vicinity of each observed point $P(\vec{r})$ at a given moment in time is sufficiently small (to the continuity limit of the dispersed medium – fluid phase). Then:

$$\rho = \lim_{\Delta V \rightarrow 0} \frac{\Delta m}{\Delta V} = \begin{cases} \rho_p & \text{for } P(\vec{r}) \in V_p \\ \rho_f & \text{for } P(\vec{r}) \in V_f \end{cases} \quad (7),$$

where it has been taken into account that the observed volume V consists of the particle volume, V_p , and the fluid volume, V_f , i.e.,

$$V = V_p + V_f \Leftrightarrow F = F_p + F_f, (V = k \cdot F) \quad (8),$$

For the particle volume concentration c_v and porosity $\bar{\epsilon}$, the following is valid:

$$\frac{\bar{c}_v}{c_v} = \frac{V_p}{V} = \frac{F_p}{F} = 1 - \frac{F_f}{F} = 1 - \frac{V_f}{V} = 1 - \bar{\epsilon} \quad (9),$$

$$F_p = \bar{c}_v \cdot F, \quad F_f = (1 - \bar{c}_v) \cdot F \quad (10).$$

From the definition of Equation (1)|(2), the immission|emission rate is as follows:

$$I(t)|E(t) = \dot{m}_p(t) = \int_{F_i|F_E} \rho(\vec{r}, t) \cdot \vec{v}_p(\vec{r}, t) \cdot \vec{n}(\vec{r}) dF = \int_{F_p} \rho_p \cdot \vec{v}_p(\vec{r}, t) \cdot \vec{n}(\vec{r}) dF = \rho_p \sum_i [\vec{v}_p(\vec{r}, t) \cdot \vec{n}(\vec{r})]_i \cdot (\Delta F_p)_i = \rho_p \cdot (\overline{\vec{v}_p(t)}) \cdot F \neq \rho_p \cdot \overline{\vec{v}_p(t)} \cdot \overline{c_v(t)} \cdot F = \overline{c_m(t)} \cdot \overline{\vec{v}_p(t)} \cdot F \quad (11),$$

where,

$[\vec{v}_p(\vec{r}, t) \cdot \vec{n}(\vec{r})]_i$ – is the projection of i -th particle velocity in the direction \vec{n} ,

$(\Delta F_p)_i$ – is the projection surface of the i -th particle normal to \vec{n} ,

taking into account that,

$$\vec{v}_p = 0 \quad \text{for } P(\vec{r}) \notin F_p \quad (12).$$

In Equations (5) and (11), in which the particle immission|emission rate is reduced to the mean values over the surface $F_{\parallel}|F_E$, attention should be drawn to the inequality sign, which emphasises that the immission|emission particle flow is not equal to the product of the product of concentration and velocity mean values over the surface $F_{\parallel}|F_E$. This product is the basis of the measurement procedures for determining the immission|emission particle flow. Thus, the initial measurement uncertainty is built-in in advance into the measurement procedures for the determination of the immission|emission particle rate. The value of the measurement uncertainty for a particular measurement procedure is proportional to the quantity ratio on the left- and right-hand sides of the inequality in Equations (5) and (11).

Generally, the particle mass concentration is determined by Equation (4). However, according to the regulations [4], a definition for the mass concentration of the pollutants is:

D.6. The mass concentration of pollutants in exhaust gases is the pollutant mass per volume unit of dis-

charged gas at a temperature of 273.15 K and a pressure of 101.325 kPa. It is obvious that this defines the mass of the discharged pollutant in the discharged gas. Thus, it is the mass flow concentration c_M :

$$c_M(t) = \frac{\dot{m}_z(t)}{\dot{V}_n(t)} = \rho_n \cdot \frac{\dot{m}_z(t)}{\dot{m}_f(t)} \quad (13),$$

where the indices denote z for the pollutant and n for the standard gas parameters (e.g., 273.15 K, 101.325 kPa). The denominator in Equation (13) is determined from the following equation:

$$\begin{aligned} \dot{V}_n(t) &= \frac{1}{\rho_n} \dot{m}_f(t) = \frac{T_n}{p_n} \cdot \int_F \frac{p(\vec{r}, t)}{T(\vec{r}, t)} \cdot \vec{v}_f(\vec{r}, t) \cdot \vec{n}(\vec{r}) dF = \\ &= \frac{T_n}{p_n} \cdot \left[\frac{p(t)}{T(t)} \cdot v_f(t) \right] \cdot F \end{aligned} \quad (14).$$

From Equations (5), (13) and (14), the mass flow concentration for the particulate matter (index: $z = p$) is:

$$c_M(t) = \frac{p_n}{T_n} \cdot \frac{\left[\frac{c_m(t) \cdot v_p(t)}{\frac{p(t)}{T(t)} \cdot v_f(t)} \right]}{\left[\frac{p(t)}{T(t)} \cdot v_f(t) \right]} \quad (15).$$

Furthermore, the volume flow concentration, c_V , for particulate matter is:

$$c_V(t) = \frac{\dot{V}_p(t)}{\dot{V}_n(t)} = \frac{\rho_n}{\rho_p} \cdot \frac{\dot{m}_p(t)}{\dot{m}_f(t)} = \frac{1}{\rho_p} \cdot c_M(t) \quad (16).$$

A concentration measurement is essential for any measurement method for determining the immission and emission quantities. In an immission measurement, that is usually the final objective: the concentration field of some area, space and the like, on the basis of which the immission rate, the rate density, and the immission dose are evaluated in relation to particular receptors. The concentration for emission monitoring and evaluating has the meaning of a subsidiary quantity in order to determine/monitor the source emission flow, i.e., its significance in terms of the environmental contamination.

2 SAMPLING OF PARTICLES IN THE DETERMINATION OF THEIR CONCENTRATIONS IN A GASEOUS ENVIRONMENT

There are two essentially different cases of sampling of particles that can be found in applications [5]: (i) the sampling of flowing particle-gas systems, (ii) the sampling of stationary particle-gas systems. A direct quotation from the English original [5]

describes the division as: (i) *sampling of flowing aerosols*, (ii) *sampling of stationary aerosols*. The correct interpretation of the term aerosol can be considered as questionable. This headword in the Croatian version of the three-language dictionary [1] is cited with following meaning:

D.7. Aerosol: a two-phase system in which the continuous phase is gaseous and the dispersed phase is liquid and/or solid; dispersed system particles have a negligible deposition velocity in the gravitational field.

In this definition, the limit of neglecting the deposition velocity is not determined and with no reason aerosols are attributed to a relatively narrow subclass of particle-fluid dispersed systems. Since during every sampling of the particle-gas system care must be taken about the influence of gravitational forces (i.e., how to avoid their influence on the measurement error), it is more correct to accept the following definition [6]:

D.8. Aerosol: a two-phase system in which solid and/or liquid particles are dispersed in a gas.

Yet, for that, as well as for any other particle system dispersed in a fluid, it should be kept in mind that its existence depends on the mutual ratio of the gravitational and carrying forces. According to such a rule, aerosols would be a subclass of a particle-fluid dispersed system, for which, approximately, the size of the dispersed solid/liquid particles is in the range (aerodynamic diameter) of 2 nm to 100 μm [6]. Essentially, such a particle size range covers aerodispersed systems, which are a subject of interest for environmental protection (air-quality protection). In accordance with the introduced classification, the sampling of the flowing gas-particle system includes aerosols that flow through pipe ducts and the like, as well as atmospheric aerosols in the presence of wind, while the sampling of the stationary gas-particle system includes aerosols in quiet conditions, including both the outside air and the air of working or indoor living spaces. In the sampling of flowing aerosols, measurement errors are mainly a consequence of particle inertia forces that condition the deviation of the particle trajectory from the streamline (Fig. 1) [7]. If the sample opening is not placed isoaxially (Fig. 1.a)), or if the sample suction velocity is higher (Fig. 1.b)) or lower (Fig. 1.c)) than the fluid velocity in the undisturbed flow, the sample particle concentration will be smaller (Fig. 1.a) and b)) or greater (Fig. 1.c)) than the real particle concentration.

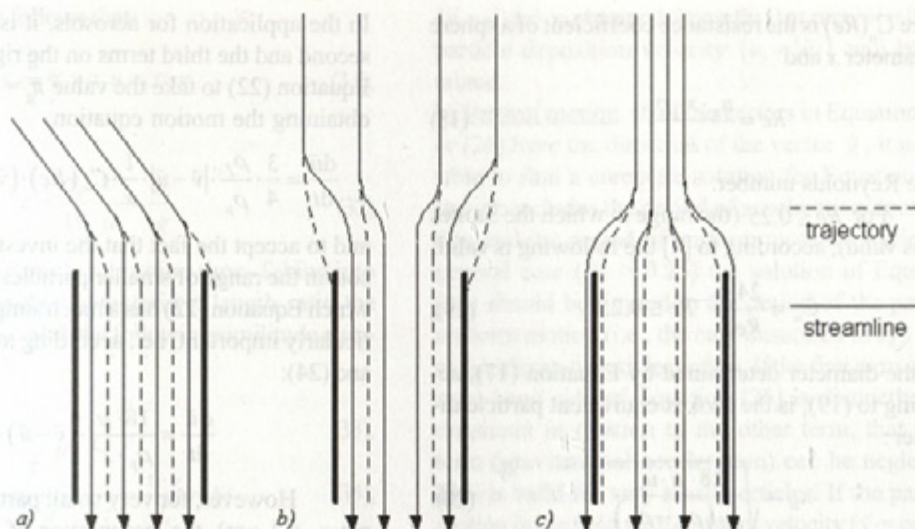


Fig. 1. Errors in the flowing aerosol sampling: a) non-isoaxial, b) non-isokinetic, c) sub-isokinetic

Therefore, sampling should be isoaxial, isokinetic and the wall of the suction pipe (probe) should be sufficiently thin.

The sampling of stationary aerosols has no analogy with the sampling of flowing aerosols because the flow field in the neighbourhood of the sampler opening in the case of the flowing fluid environment (Fig. 1) is completely different from the flow field created around the sampler opening in the case of the stationary fluid environment (Fig. 2). In addition, this type of sampling has been less frequently investigated than the sampling of flowing aerosols. Regardless of the difference in the fluid flow field created in the two mentioned opposite cases in the neighbourhood of the sampler input opening, the increase in the measurement error of aerosol sampling, compared to other (gaseous) pollutants, is a consequence of the particle trajectory in the fluid environment.

3 PARTICLE TRAJECTORY PROPERTIES

The measure of the particle size is its equivalent diameter [1]:

D.9. The equivalent diameter is the diameter of a round particle that has the same geometrical, optical, electrical or aerodynamic behaviour as the tested particle.

The hydrodynamic/aerodynamic particle behaviour is of major importance for the sampling of aerosols. As such, the measure of the particle size is its diameter, the Stokes diameter or the aerodynamic diameter. If u_s denotes the stationary deposition velocity of some observed particle in an infinitely spread fluid environment at rest under the action of gravitational force, the equivalent diameter of that particle in relation to the deposition velocity comes to:

$$x_s = x = \frac{3}{4} \cdot C_w(Re) \cdot \frac{\rho_f}{(\rho_p - \rho_f) \cdot g} \cdot u_s^2 \quad (17),$$

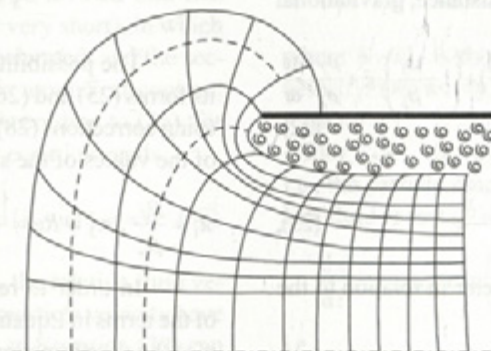


Fig. 2. Flow field during suction from a stationary fluid environment

where $C_w(Re)$ is the resistance coefficient of a sphere of diameter x and

$$Re = \frac{u_s \cdot x \cdot \rho_f}{\mu} \quad (18)$$

is the Reynolds number.

For $Re \leq 0.25$ (the range in which the Stokes law is valid), according to [8] the following is valid:

$$C_w = \frac{24}{Re}, \quad Re \leq 0.25 \quad (19),$$

and the diameter determined by Equation (17), according to (19), is the Stokes equivalent particle diameter:

$$x_{st} = \sqrt{\frac{18 \cdot \mu \cdot u_s}{g \cdot (\rho_p - \rho_f)}} \quad (20).$$

Regarding the range in which the Stokes law is valid (Equation (19)), Equation (20), in usual fluid conditions, can be applied up to $x_{st} < 50 \mu\text{m}$ for air, and up to $x_{st} < 80 \mu\text{m}$ for water. When aerosols are concerned, one can also use the aerodynamic equivalent diameter x_{ae} for which the particle deposition velocity is reduced to the Stokes sphere deposition velocity at $\rho_p - \rho_f = 1 \text{ g/cm}^3$, i.e.,

$$x_{ae} = x_{st} \cdot \sqrt{\rho_p - \rho_f} \quad (21).$$

Also, in the application of Equations (17), (20) and (21) for aerosols, because $\rho_f / \rho_p \approx 10^{-3}$, ρ_f is neglected in most cases.

A starting model for the aerosol sampling analysis in order to determine the corresponding immission and emission quantities is based on the following assumptions:

- particles are considered individually, without taking into account their mutual influence,
- the particle motion equation is set on the basis of the equilibrium of inertia, resistance, gravitational and pressure forces, i.e.,

$$\frac{d\vec{u}}{dt} = C_w(Re) \cdot F_p \cdot \frac{\rho_f}{2 \cdot m} \cdot |\vec{v} - \vec{u}| \cdot (\vec{v} - \vec{u}) + \left(1 - \frac{\rho_f}{\rho_p}\right) \cdot \vec{g} + \frac{\rho_f}{\rho_p} \cdot \frac{d\vec{v}}{dt} \quad (22),$$

where now,

$$Re = \frac{|\vec{v} - \vec{u}| \cdot \rho_f \cdot x}{\mu} \quad (23),$$

where x is the equivalent diameter in relation to the deposition velocity, and

$$m = \rho_p \cdot \frac{\pi \cdot x^3}{6}, \quad F_p = \frac{\pi \cdot x^2}{4} \quad (24).$$

In the application for aerosols, it is justified in the second and the third terms on the right-hand side of Equation (22) to take the value $\pi_1 = \rho_f / \rho_p \approx 0$, thus obtaining the motion equation,

$$\frac{d\vec{u}}{dt} = \frac{3}{4} \cdot \frac{\rho_f}{\rho_p} \cdot |\vec{v} - \vec{u}| \cdot \frac{1}{x} \cdot C_w(Re) \cdot (\vec{v} - \vec{u}) + \vec{g} \quad (25),$$

and to accept the fact that the investigation of aerosols in the range of smaller particles ($Re < 0.25$), for which Equation (22) has a much simpler form, is particularly important, i.e., according to (19), (22), (23) and (24):

$$\frac{d\vec{u}}{dt} = \frac{18 \cdot \mu}{\rho_p \cdot x^2} \cdot (\vec{v} - \vec{u}) + \vec{g} \quad (26).$$

However, for very small particles (for example $x_{st} < 1 \mu\text{m}$), the assumption of a fluid environment continuity gradually retreats as their magnitudes approach the magnitude of the free trajectory of fluid molecules, λ (for air in standard conditions $\lambda \approx 65 \text{ nm}$). Then the particle resistance coefficient, C_w , depends on the Knudsen number

$$Kn = \frac{\lambda}{x} \quad (27),$$

so, the following is valid (for: $0.1 < Kn < 1000$; $Re < 0.25$):

$$C_w = \frac{24}{Re} \cdot \left\{ 1 + \frac{\lambda}{x} \cdot \left[2.514 + 0.800 \cdot \exp\left(-0.55 \cdot \frac{\lambda}{x}\right) \right] \right\}^{-1} = \frac{24}{Re} \cdot Cu^{-1} \quad (28),$$

where Cu denotes the Cunningham correction factor. When applying Equations (27) and (28) one should know how the equivalent particle diameter, x , has been determined because, due to the importance of the resistance coefficient, C_w , for the deposition velocity, the following is valid:

$$x = x_{st} \cdot \sqrt{\frac{1}{Cu}} \quad (29).$$

The possibility of reducing Equation (22) to its forms (25) and (26), and the possible necessity of using corrections (28) and (29), is validated by means of the values of the similitude numbers:

$$\pi_1 = \frac{\rho_f}{\rho_p}, \quad \pi_2 = Re = \frac{|\vec{v} - \vec{u}| \cdot \rho_f \cdot x}{\mu}, \quad \pi_3 = Kn = \frac{\lambda}{x} \quad (30).$$

In order to reach a complete understanding of the terms in Equation (26) it is necessary to recognize the remaining important similitude numbers. By applying the integral analogy procedure [9], from

Equation (26) it follows that:

$$\tau \cdot \frac{u}{l} \propto v \propto u \propto \tau \cdot g \quad (31),$$

where

$$\tau = \frac{\rho_p \cdot x^2}{18 \cdot \mu} = \frac{u}{g} \quad (32)$$

is the so-called particle relaxation time. Taking into account that for the characteristic length ratio the relation $L = v \cdot t$ is valid, the following similitude numbers are derived:

$$\pi_4 = \frac{u}{v} \quad (33),$$

$$\pi_5 = \frac{\tau \cdot u}{L} = \frac{\tau}{t} = \frac{\tau \cdot v}{L} = St \quad (34),$$

$$\pi_6 = \frac{\tau \cdot g}{v} = \frac{u_s}{v} = \frac{\tau \cdot v}{L} \cdot \frac{g \cdot L}{v^2} = St \cdot Fr^{-2} \quad (35),$$

where

$$St = \frac{\tau \cdot v}{L} = \frac{\rho_p \cdot x^2 \cdot v}{18 \cdot \mu \cdot L} \quad (36)$$

is the Stokes number, and

$$Fr = \frac{v}{\sqrt{g \cdot L}} \quad (37)$$

is the Froude number.

In a general case, Equations (25) or (26) cannot be analytically solved. To solve them it would be necessary to know the fluid velocity field $\vec{v} = \vec{v}(\vec{r})$, and then the solution could be obtained numerically (for example, the Runge-Kutta method). However, possible analytical solutions, for the simplest cases, give very important data concerning the behaviour of aerosol particles in sampling procedures.

a) **Uniform particle motion.** If the fluid velocity \vec{v} is constant, particle motion can be divided into two periods. The first one (usually very short), in which a particle is decelerated or accelerated, and the second one, in which a particle is moving at constant speed, i.e., when $d\vec{u}/dt = 0$. According to (25), for the second period the motion equation reads,

$$\frac{3}{4} \cdot \frac{\rho_f}{\rho_p} \cdot |\vec{v} - \vec{u}| \cdot \frac{1}{x} \cdot C_w(Re) \cdot (\vec{v} - \vec{u}) + \vec{g} = 0 \quad (38).$$

Obviously, in this case, the relative fluid velocity (here, it is a gas) and the particle velocity have the direction of the vector \vec{g} , so Equation (38) can be written in scalar form, from which the vector

$(\vec{v} - \vec{u}) \parallel \vec{g}$ is obtained. For a fluid at rest $|\vec{v}| = 0$, the particle deposition velocity ($u_d = |\vec{u}|$) will be obtained.

b) **Vertical motion.** If all the vectors in Equation (25) or (26) have the direction of the vector \vec{g} , it is possible to find a complete solution for Equation (26) (which includes the period of acceleration/deceleration and the period of uniform motion), while in a general case ($Re > 0.25$) the solution of Equation (25) should be limited to the period of the particle uniform motion (i.e., the case described in a)).

c) **Accelerated particle motion.** If the first term on the right-hand side of Equation (25) is distinctly predominant in relation to the other term, that other term (gravitational acceleration) can be neglected. This is valid for very small particles. If the particle motion in the field with constant velocity ($\vec{v} = \text{const.}$) is concerned, the particle motion equation becomes,

$$\frac{d(\vec{v} - \vec{u})}{dt} = -\frac{3}{4} \cdot \frac{\rho_f}{\rho_p} \cdot |\vec{v} - \vec{u}| \cdot \frac{1}{x} \cdot C_w(Re) \cdot (\vec{v} - \vec{u}) \quad (39),$$

from which it follows that a change in the relative fluid and particle velocities can happen only in the direction of that relative velocity, i.e., only the intensity of the relative velocity can change, not its direction. The case for the range $Re \leq 0.25$ (i.e., the range for very small particles) is of particular importance. Then, the differential Equation (39) assumes the form

$$\frac{d(\vec{v} - \vec{u})}{dt} = -\frac{18 \cdot \mu}{\rho_p \cdot x^2} \cdot (\vec{v} - \vec{u}) = -\frac{1}{\tau} \cdot (\vec{v} - \vec{u}) \quad (40),$$

and the equation for the intensity of the relative velocity $(\vec{v} - \vec{u})$ follows,

$$\frac{d|\vec{v} - \vec{u}|}{|\vec{v} - \vec{u}|} = -\frac{1}{\tau} dt \quad (41),$$

the solution of which is,

$$|\vec{v} - \vec{u}| = |\vec{v} - \vec{u}|_0 \cdot \exp\left(-\frac{t}{\tau}\right) \quad (42),$$

where $|\vec{v} - \vec{u}|_0$ is the initial intensity of the relative velocity. Obviously,

$$\text{for } t = \tau \quad |\vec{v} - \vec{u}| = (1/e) \cdot |\vec{v} - \vec{u}|_0 \text{ is valid} \quad (43),$$

$$\text{for } t \rightarrow \infty \quad |\vec{v} - \vec{u}| = 0 \text{ is valid} \quad (44),$$

i.e., the particle assumes the fluid velocity.

In a fluid at rest ($\vec{v} = 0$), according to (42),

$$\frac{ds}{dt} = u = u_0 \cdot \exp\left(-\frac{t}{\tau}\right), \quad (u = |\vec{u}|, u_0 = |\vec{u}|_0) \quad (45),$$

i.e.,

$$s = u_0 \cdot \tau \cdot \left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \quad (46),$$

from where, for $t \rightarrow \infty$, the so-called stopping particle path (the penetration of the particle into the fluid at the starting velocity u_0) is obtained:

$$s_{\infty} = u_0 \cdot \tau \quad (47).$$

Thus, during the sampling of aerosols the ratio s_{∞}/D is very important because,

$$St = \frac{s_{\infty}}{D} = \frac{u_0 \cdot \rho_p \cdot x^2}{18 \cdot \mu \cdot D} \quad (48),$$

where D is the diameter of the suction probe opening.

However, as a rule, the upper limit of the applicability of equations derived from the condition $Re > 0.25$ (which is, for the air, approximately equivalent to the condition $x_{st} < 50 \mu\text{m}$) is not taken into account in applications. For the range $Re > 0.25$, the relaxation time $\tau = \tau^*$ should be defined directly from Equation (25), so then,

$$\tau^* = \frac{4}{3} \cdot \frac{\rho_p \cdot x}{\rho_f \cdot |\vec{v} - \vec{u}| \cdot C_{\infty}(Re)} \quad (49),$$

and the stopping trajectory,

$$s_{\infty} = u_0 \cdot \tau^* = u_0 \cdot \tau \cdot \varphi(Re_0) \quad (50),$$

where $\varphi(Re_0)$ is the correction function depending on the Reynolds number,

$$Re_0 = \frac{u_0 \cdot x \cdot \rho_f}{\mu} \quad (51),$$

the values of which are given in Table 1.

Table 1. Correction function values

Re_0	10^{-1}	10^0	10^1	10^2	10^3
$\varphi(Re_0)$	1.00	0.97	0.72	0.38	0.17

According to the correction function values, it follows that for $Re > 0.25$ the calculation of the stopping path from Equation (47) would give overestimated values.

4 SAMPLING WHEN DETERMINING THE EMISSION AND IMMISSION QUANTITIES

4.1 Emission measurements

Since it is either almost impossible or very difficult to correctly measure the pollutant emission at corresponding points of the minimum enveloping

surface around the source (definition D.5), in the case of point sources, the emission measurements are best conducted on the discharge lines (e.g., smoke ducts, stacks, various exhaust pipes and the like). Generally, such measurements are particularly important in fossil-fuel fired power generation facilities, district heating and the chemical industry. If there are no reverse air flows or particle depositions or similar phenomena, i.e., generally, if there is no source and sink in the discharge conduit, then the below applies for steady-state conditions (Fig. 3):

$$\dot{m}_p = \text{const}(F_E), \quad \dot{m}_g = \text{const}(F_E) \quad (52),$$

i.e., as from Equations (11) and (14):

$$c_M = \text{const}(F_E), \quad c_V = \text{const}(F_E) \quad (53),$$

it would generally be irrelevant where (in which cross-section of the discharge duct) the emissions are measured. Even a possible reverse flow of air in the discharge line and/or gas discharge downstream of the measurement point and/or the deposition of particles upstream of the measurement point, and the like, do not affect emission quantities, which are, according to the regulations, reduced to dry gases, their standard condition and specified oxygen percentages. The selection of an appropriate measurement cross-section is actually determined by the limitations imposed by the measurement procedures and equipment. Specified rules (or guidelines) pertaining to the specified monitoring of emission usually regulate the selection of an appropriate measurement cross-section. Particularly important is the distance from the upstream and/or downstream sources of the fluid flow disturbance (expressed through a hydraulic diameter multiple) ([10] to [12]) and, for particles, the properties related to their inertial characteristics: possible deposition (the advantage of vertical in relation to horizontal ducts); a possibly more pronounced non-uniform particle concentration across the section of discharge ducts, for example, after flow disturbances; the dependence of inertial effects on the particle granulometric composition and the particle density [12].

In applications, when monitoring pollutant emissions into the air, the selected conditions are usually those that enable a rational use of the available measurement techniques and also enable simplifications, while having an acceptable effect on

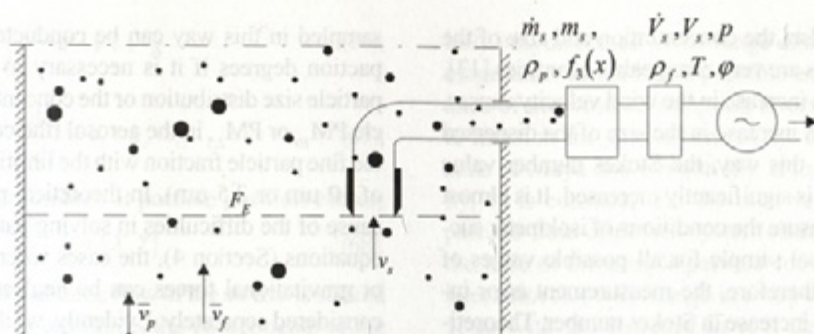


Fig. 3. Arrangement of the gravimetric and photometric measurement of particulate emission quantities

the reliability of the final results. These are as follows:

(i) Selection of the measurement surface, F_E , in a plane of the discharge section where the following applies:

$$\vec{v}_p \parallel \vec{v}_f \parallel \vec{n} \quad (54)$$

and at points at which there are no (local) particle concentrations and/or gas velocity gradients in the direction of the unit vector \vec{n} .

(ii) The pressure $p(t)$ and the temperature $T(t)$ are measured at a single representative point on the surface, F_E (with a possible exception for scientific purposes), i.e., they are accepted as invariable in the average plane points.

(iii) The following is accepted (see Equations (5) and (11)):

$$\begin{aligned} \overline{c_m(t) \cdot v_p(t)} &= \overline{c_m(t)} \cdot \overline{v_p(t)} \\ \overline{v_p(t) \cdot c_v(t)} &= \overline{v_p(t)} \cdot \overline{c_v(t)} \end{aligned} \quad (55)$$

Obviously, compared to gaseous pollutants, it is more difficult to satisfy conditions (i) and (iii) when measuring particulate emission because the particles are exposed to the inertia forces.

Considering conditions (i)–(iii), Equations (5), (11), (14) and (15) may be simplified for the discharge ducts and, consequently, a simpler measurement procedure can be applied. For the said conditions, the following applies to the discharge ducts:

$$\dot{m}_p(t) = \overline{c_m(t)} \cdot \overline{v_p(t)} \cdot F_E \quad (56)$$

$$c_M(t) = \frac{p_n}{p(t)} \cdot \frac{T(t)}{T_n} \cdot \frac{v_p(t)}{v_f(t)} \cdot \overline{c_m(t)} \quad (57)$$

An important characteristic of gravimetry is the acceptance of the iso-kinetic suction of particulate matter samples. At the i -th point of the measurement plane, F_E (Fig. 3), the following is chosen:

$$v_{pi} = v_{fi} \quad (58)$$

With the standardized measurement procedure, and the already introduced simplifications (described, for example, in [11]), the gravimetric mass concentration, c_{GR} , will be:

$$c_{GR} = \rho_n \cdot \frac{m_p}{m_f} = \frac{p_n}{p} \cdot \frac{T}{T_n} \cdot \frac{\sum_i (v_{pi} \cdot c_{mi}) \cdot \Delta F_{Ei} \cdot \Delta t_i}{\sum_i v_{fi} \cdot \Delta F_{Ei} \cdot \Delta t_i} \quad (59)$$

and with the specified condition,

$$\Delta F_{Ei} = \text{inv}(i), \quad \Delta t_i = \text{inv}(i) \quad (60)$$

this gives:

$$c_{GR} = \frac{p_n}{p} \cdot \frac{T}{T_n} \cdot \frac{(\overline{v_p \cdot c_m})}{v_f} \quad (61)$$

where p and T are either the average time values during the period $\sum \Delta t_i$ or the measurement has been conducted under (nearly) steady-state conditions. However, only if,

$$v_{pi} \approx v_{fi} \quad (62)$$

is assumed, it will give,

$$c_{GR} = \frac{p_n}{p} \cdot \frac{T}{T_n} \cdot \frac{(\overline{v_f \cdot c_m})}{v_f} = \overline{c_m} \quad (63)$$

i.e., from Equation (61), and taking into account Equations (5), (11) and (15), the emission gravimetry corrects the procedure of averaging over the points in the plane F_E . For emission flow (averaged for the period $\sum \Delta t_i$), the following applies:

$$\dot{m}_p = c_{GR} \cdot \frac{\dot{m}_f}{\rho_n} = (\overline{v_p \cdot c_m}) \cdot F_E \approx (\overline{v_f \cdot c_m}) \cdot F_E \approx \overline{v_f} \cdot \overline{c_m} \cdot F_E \quad (64)$$

4.2 Immission measurements

The sampling of aerosols is a particularly complex procedure if it is carried out in outdoor conditions, because the intensity, line and direction of

the wind and, also, the concentration and size of the flowing particles are very changeable quantities [13]. For example, an increase in the wind velocity causes, in most cases, an increase in the size of the dispersed particles, so, in this way, the Stokes number value (Equation (48)) is significantly increased. It is almost impossible to ensure the conditions of isokinetic suction of an aerosol sample for all possible values of wind velocity; therefore, the measurement error increases with the increase in Stokes number. Theoretical approaches to the problem of aerosol sampling are reduced to the range of laminar fluid flow, although, in the real atmosphere, the flow of the air is more or less turbulent. The necessity of simulating the flows of monodispersed particles with a constant concentration accounts for the limitations and relatively large errors of the experimental approach. In applications, for routine emission measurements, suction is usually carried out through an opening with a section mounted in the horizontal plane, in the top-to-bottom direction. In order to make the direct deposition of (especially big) particles in the suction opening impossible, and to prevent the penetration of atmospheric precipitation, the suction opening is covered with plates of different shapes, placed at a small distance from the opening. In this way, a relatively efficacious suction of particles of approximately 100 μm is realized, and there is only a slight probability of the suction of significantly larger particles. The aerosol

sampled in this way can be conducted through impaction degrees if it is necessary to determine the particle size distribution or the concentration of particle PM_{10} or $\text{PM}_{2.5}$ in the aerosol (the concentration of the fine particle fraction with the limiting particle size of 10 μm or 2.5 μm). In theoretical procedures, because of the difficulties in solving particle trajectory equations (Section 4), the cases where either inertia or gravitational forces can be neglected are usually considered separately. Evidently, while sampling, no inertial particles with a probe/pipe placed in the vertical line, at the suction velocity v_s , the particle concentration ($1 \pm u_s/v_s$) times changed ("+"; top-to-bottom; "-" ; bottom-to-top) is obtained in the sample.

The theoretical solution of the case of aerosol suction through a point sink placed in a vertical plane (wall) ([5] and [7]) is of particular importance. The starting point of the consideration is a two-dimensional case (Fig. 4): the aerosol is sucked in through an infinitely narrow clearance of infinite length (point 0) from the half-space (right half-plane in Fig. 4) limited by the wall plane. The differential equation of the motion of small particles ($Re \leq 0.25$), according to (26) and (32), is,

$$\frac{d\vec{u}}{dt} = \frac{1}{\tau} \cdot (\vec{v} - \vec{u}) + \vec{g}, \quad \left(\tau = \frac{u_s}{g} \right) \quad (65).$$

Neglecting the inertia forces, the following is valid:

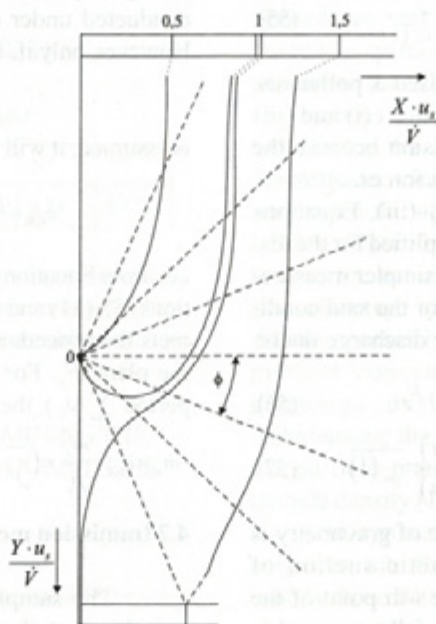


Fig. 4. Sampling of aerosols through an infinitely narrow clearance

$$\vec{u} = \vec{v} + \tau \cdot \vec{g} \quad (66)$$

i.e.,

$$\frac{d\xi_i}{dt} = v_i + u_i \cdot \delta_{i2} \quad (67)$$

where ξ_i are coordinates of particle position vector,

$$\xi_i = \{X, Y\} \quad (68)$$

If \dot{V} is the volume flow of the air that is sucked per unit length of clearance, the components of the air velocity vector are (Fig. 4):

$$v_i = \left\{ -\frac{\dot{V} \cdot X}{R^2 \cdot \pi}, -\frac{\dot{V} \cdot Y}{R^2 \cdot \pi} \right\}, \quad (R^2 = X^2 + Y^2) \quad (69)$$

System (67) reduces to the following differential equation,

$$\frac{dY}{dX} = \frac{Y}{X} - \frac{\pi \cdot u_x}{\dot{V}} \cdot \frac{X^2 + Y^2}{X} \quad (70)$$

i.e.,

$$d\left(\frac{Y}{X}\right) = -\frac{\pi \cdot u_x}{\dot{V}} \cdot \left[1 + \left(\frac{Y}{X}\right)^2\right] \cdot dX \quad (71)$$

with the solution,

$$\Phi = \frac{\pi \cdot u_x}{\dot{V}} \cdot [X_0 - X], \quad \Phi = \arctg\left(\frac{Y}{X}\right) \quad (72)$$

where X_0 is the particle initial position for $Y = -\infty$.

In terms of the obtained trajectories, the particle trajectory for which $X_0 \cdot u_x / \dot{V} = 1$ separates the particles that will be sucked from those that will miss the clearance. Consequently, all the particles, which for $Y = -\infty$ started from the length $L = \dot{V} / (1 \cdot u_x)$, pass through the unit of clearance length. Then, for $Y = -\infty$, particles move only at the velocity u_x , so if c is their concentration, the mass flow through the surface $L \cdot 1$ amounts to $\dot{m} = c \cdot u_x \cdot 1 \cdot L = c \cdot u_x \cdot 1 \cdot \dot{V} / (1 \cdot u_x) = c \cdot \dot{V}$. The concentration of particles sucked through the clearance is exactly \dot{m} / \dot{V} , i.e., it is equal to the initial concentration. Obviously, it is clear (Fig. 4) that inertial particles depart from these trajectories and that they either run into the wall under the clearance or keep on moving in the positive direction of the Y axis. Consequently, the final result is a decrease in the sample concentration. The magnitude of the deviation is exactly proportional to the stopping path $s_{\infty} = u_x \cdot \tau$. Because of this, the suction velocity should usually be several times higher than the deposition velocity, but then the question of the representative quality of the deposition velocity still needs to be dealt with because aerosol particles are regu-

larly polydispersed in the range of several orders of magnitude. Regarding a possible exceptional influence of the wind on sampling errors, it is important to mention the conclusions of the experimental results of Maya and Druetta [5]: if the suction velocity, v_s , is constant, and the inlet velocity, v , of the particle-fluid dispersed system changes from 0 to v_s , the ratio of the sample particle concentration to the inlet aerosol A will change in a way that for $v = 0$, $A = 1$, so with the increase in v , A decreases, passes through a minimum and again, for $v = v_s$, assumes the value of $A = 1$. It should be pointed out that the departure of the value A from unity significantly decreases with the decrease of the particle size and is practically negligible for a particle size of approximately $1 \mu\text{m}$.

5 CONCLUSION

In the group of measurement procedures intended for the determination of immission and emission quantities of substances considered as air pollutants, the measurement procedures for the determination of quantity, the condition and properties of the particle-fluid dispersed systems have particular significance because these procedures are subject to a significantly greater measurement uncertainty than the same measurement procedures intended for the determination of the immission and emission quantities of other air pollutants. Because of the discrete particle distribution in space, the definition of particle concentration in a gaseous environment demands a two-pronged approach: either by taking into account the discrete characteristics of particles, or by accepting the assumption of their continuous distribution – according to the conditions of the continuous environment. Using both the above mentioned approaches, the definition equations for the immission and emission flow are reduced to analogue expressions that are the basis for the corresponding measurement procedures. In these expressions it is necessary to accept approaches in relation to the averaging of the measurement quantities per surface of particle transition (emission/emission surface). In this way, the measurement uncertainty is built-in in advance.

The greatest cause of measurement uncertainty is the non-representative quality of the particle sample, as a consequence of the inertial properties of the particles, i.e., the impossibility of real-

izing the condition of the isoaxial and/or isokinetic sample suction, and the difference between the particle and the gas velocity vectors inside the sucked control volume of the particle-gas system. Regarding the fluid flow field that is formed in the neighbourhood of the suction opening, the difference between the sampling of the stationary and the flowing particle-gas system is of crucial importance because in the former and the latter cases the particle trajectories have a qualitatively different shape and hence a different demonstration of inertial action.

The immission monitoring of air pollution with particles is particularly subject to sampling errors. In this case, the measurement uncertainty decreases with the particle size decrease, so the regulatory evaluation of the air quality with respect to pollution with particles by using the fraction PM_{10} (the concentration of the fine particle fraction with a limiting particle size of $10 \mu m$), as recently introduced in the European Union, is more convenient from the point of view of measurement uncertainty in relation to the former evaluations carried out by means of the concentration of the total amount of flowing particles.

6 NOMENCLATURE

\bar{a}	average of variable a
\dot{a}	time derivation of variable a
c	concentration
$const(a)$	constant concerning the choice of a
$E(t)$	emission rate
$I(t)$	immission rate
F	surface
$inv(a)$	invariance concerning a
k	constant
L	length
m	mass
p	pressure
\vec{r}	position vector
t	time
T	temperature
u	particle velocity
v	velocity
V	volume
x	equivalent particle diameter

δ	Kronecker symbol: $\delta_{ij} = \begin{cases} 1 & (i = j) \\ 0 & (i \neq j) \end{cases}$
ε	porosity
\in	is an element of
μ	dynamic viscosity
ρ	density
τ	particle relaxation time

Indices

E	emission
I	immission
f	fluid/gas
g	gas
GR	gravimetry
m, M	mass
n	standard parameters
N	number
p	particle
s	sample; deposition
v, V	volume

7 LITERATURE

- [1] HRN ISO 4225: 1997, Air quality – General views – Dictionary (ISO 4225: 1994), Threelinguall edition, Zagreb, 1997 – in Croatian.
- [2] ISO/TR 4227, Planning of ambient air quality monitoring (1989) ISO, Genève.
- [3] Barbalić N., Marijan G., Bilić Ž. (2001) Conditions and phenomena which a priori limit the confidence of continuous measurement of particulate emission in the air, *12th IUAPPA world clean air and environment congress*. Proceedings: ref. TS1-72c, Seoul.
- [4] Regulation of limiting values for pollutant emission from stationary sources, *Narodne novine* No. 140, pp. 4406 – 4425, 1997; *Narodne novine*, No. 105, pp. 4008 – 4096, 2002.
- [5] Fuchs N.A. (1975) Sampling of aerosols, *Atmospheric Environment* 9, pp. 697-707, 1975.
- [6] Šega K. (2004) Flowing particles, *Gospodarstvo i okoliš* 12, No. 66, pp. 11-16, 2004.
- [7] Fuchs N.A. (1955) *Mehanika aerosoli*, Izd. AN SSSR, Moskva.
- [8] Löffler F. (1988) *Staubabscheiden*, Georg Thieme Verlag, Stuttgart – New York.
- [9] Smolik J. (1977) *Odlučování tuhých částic*, Fakulta strojní, ČVUT, Praha.

- [10] BS 893: Measurement of the concentration of particulate matter in ducts carrying gases, 1978; BS 3405: Measurement of particulate emission including grit and dust (simplified method), 1983; HRN ISO 9096: 1997, Stationary source emissions – Determination of concentration and mass flow rate of particulate material in gas-carrying ducts – Manual gravimetric method (ISO 9096: 1992), *State Office for Standardization and Metrology*, Zagreb, 1997.
- [11] Bilić Ž., Barbalić N. (1985) Gravimetric procedure for concentration and mass flow measurements of solid particles in flowing gases in flow ducts, *Recommendation SDCVJ 301*, SDCVJ, Sarajevo – in Croatian.
- [12] Hawksley P. G. W., Badzioch S., Blackett J. H. (1961) Measurements of solids in the flue gases, *The British Coal Utilization Research Association*, Leatherhead.
- [13] Belyaev S.P., Levin L.M. (1974) Techniques for collection of representative aerosol samples, *Aerosol Science* 5, pp. 325-328, 1974.

Author's Addresses:

Doc. Dr. Nastia Degiuli
University of Zagreb
Faculty of Mechanical Engineering and
Naval Architecture
Ivana Lučića 5
10000 Zagreb, Croatia
nastia.degiuli@fsb.hr

Prof. Dr. Nikola Barbalić
Goran Marijan
Hrvatska elektroprivreda
Sektor za termoelektrane
Ulica grada Vukovara 37
10000 Zagreb, Croatia
goran.marijan@hep.hr

Prejeto:
Received: 6.6.2006

Sprejeto:
Accepted: 25.4.2007

Odrpo za diskusiju: 1 leto
Open for discussion: 1 year