



Evaluation of Selected Pollutants and Measures to Reduce Their Impacts on Health in Military Workplaces

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The paper describes the measurement of contamination by selected pollutants such as explosives and nanoparticles in military workplaces. A scanning mobility particle sizer and a functional sample of a portable device for rapid analysis of explosives and nanoparticles were exploited for the evaluation. The portable device has been designed and put into service and it consists of two parts: the original microcolumn miniaturized liquid chromatograph and a unique chemiluminescence detector. Pollutants were measured in the air. The evaluation of harmful effects was focused on health risks connected with explosives and nanoparticles. The contribution indicates steps to decrease the impact on health of soldiers. The analysis of literature suggested that a number of methods using air sampling did not lead to a reproducible determination of pollutants. The study presents the equipment that eliminates the above mentioned problem and enables a rapid, reproducible and reliable collection of gas samples. A great advantage of the portable device is that it enables multiple repetition of the experiment. The second part of the study was dedicated to the issue of aerosols with an emphasis on ultrafine aerosols - nanoparticles.

1. Introduction

Chemical survey represents a set of activities leading to the detection, characterization, identification and determination of dangerous chemicals (DC) and chemical warfare agents (CWA). In the case of release of such particles into the environment, the detection is realised in field conditions. Measured data, as well as other identified circumstances, are interpreted in order to identify typical hazards, design procedures to prevent the spread of threats, to reduce risks and also to assure the protection of intervening persons (MV-GŘ HZS ČR, 2006).

As it is evident from the definition of chemical exploration, it is a very discerning activity that poses great demands on both: the detection technique and the ability of personnel to operate with analytical equipment. These activities are performed in competence of the Ministry of Defence and the Ministry of the Interior of the Czech Republic within the civil protection (eg. decontamination).

The modern trend of development of analytical methods for the detection of energetic materials in the Armed Forces of the Czech Republic is moving towards the detection of vapours and aerosols in the ambient air. Currently, these solid or liquid aerosols are referred to as "particulate material" (PM) (Li and Mao, 2015). Parameters commonly used to describe aerosols (concentration, chemical composition, etc.) are extended by other values, such as the number of aerosol particles, their size and shape. The importance of new parameters increases with the decreasing size of a particle. Of particular importance are so-called nanoparticles in the range of 1100 nm. The prefix "nano" represents especially the different physical, chemical and biological properties in comparison with the materials within the macroscale. Physicochemical features of nanomaterials primarily depend on the specific surface area and surface energy of these ultrafine particles, while the chemical composition influences their properties to a lesser extent. In terms of the impact on human health, the particle size is crucial for their role and behaviour in the organism (eg. affecting the place where the particle settles down in the respiratory tract).

Nanoparticles are formed naturally, eg. during volcanic eruptions, dust storms and wildfires (Buzea et al., 2007). These have always been part of the environment. Due to human activities, their concentration has however significantly increased (Obersdörster et al., 2005, Roy et al., 2014). Among their most important resources are currently included: internal combustion engines, thermal power plants, smelters and other combustion processes (coal and wood for heating households and industrial production) (Grigoriu et al., 2012, Rönkkö et al., 2014). With a rapid development of nanotechnology in recent decades, the amount of nanoparticles has also increasingly risen due to deliberate industrial production of nanomaterials. These substances can be easily released to the environment not only during production of nanomaterials, but also during their use and their subsequent decomposition (Guiot et al., 2009, Biskos and Schmidt-Ott, 2012). Till now, there has been no available method for measuring ultrafine particles within the entire spectrum of their sizes. There is no single measurement principle that would obtain all the required parameters. The greatest perspective is nowadays instant sorting of particles (for example real-time sizing) where both the inertial forces of particles with their optical properties and measurement of the behaviour of particles in an electric field are used. A summary of these principles is exploited in the most used device: the scanning mobility particle sizer (SMPS).

1.1 Overview of the Issue

The most common way of obtaining gaseous substances is air sampling which is contaminated with an unknown chemical substance (e.g. energetic compounds in the form of vapours or aerosols). In the conventional procedures chemical compounds in the air are preconcentrated by absorption in so-called "impingers" or are collected on special filters. The word impinger relates to a device absorbing dusty substances from the air. Impingers are not appropriate for concentrations of less than ppb since they contain relatively large amounts of liquid, reducing the degree of enrichment and the sensitivity of analytical methods. The degree of enrichment means the ratio of the separated substances in the mixture before and after separation, specifying the loss of material during the separation process. Another disadvantage is the necessity to suck often large volumes of the air during concentration, while this step causes significant losses of pollutants already absorbed in the liquid. The reliability of determination is also affected by the presence of aerosols and the necessity of using a filter that leads to a distortion of results (Večeřa et al., 2011). The use of filters is limited by their sorption capacity, while the main problem is the loss of volatiles that occurs during the sucking phase.

Currently, gases and aerosols containing chemicals can be captured in denuder (thin tube whose inner wall is covered with a sorbent catching the gaseous components, meanwhile the aerosol particles are drifted out from the device). Denuders are exploited in analytics of trace pollutant concentrations in the air as well as in the separation of gaseous pollutants from substances in the condensed phase. By performing this method of analysis, the sorbent is sampled, transported to and stored in the laboratory. After that, the analyte undergoes thermal desorption or extraction and is analysed by gas chromatography, combined gas chromatography or mass spectrometry. This relatively simple procedure fails when determining thermally unstable organic compounds (e.g. organic compounds containing sulphur in the molecule or biogenic substances such as terpenes). During the determination of volatile organic compounds in the atmosphere, the usage of dry denuders requires application of activated carbon, Tenax, and various silicon compounds. In most cases, organic compounds are thermally desorbed or extracted using a suitable solvent and analysed (Večeřa et al., 2011). Common methodological disadvantage of all above processes is discontinuity of determination. This means that only integrated information values of the analyte content in the atmosphere at a certain time interval are received (Večeřa et al., 2011). The above mentioned detection methods are not able to capture and select aerosols in accurately specified ranges of nanometers.

2. The practical part

The absence of pore clogging of the membrane provides a so-called wet denuder, wherein the absorbed liquid is in direct contact with the analysed air. The simplest version of the Wet Effluent Diffusion Denuder (WEDD) is illustrated in Figure 1. It is a cylindrical borosilicate tube whose inner wall is formed by a porous layer of modified soft glass. The inner wall covered with a layer of porous soft glass is highly wettable. Absorbent medium flows down the wall in a thin film due to gravity, whereas the analysed air moves upwards in counter current laminar flow (Večeřa et al., 2011).

In more complex arrangements, WEDD rotating denuder may be exploited. This type of denuder is rotated along its longitudinal axis and the absorption liquid is maintained at the "active" side of denuder by centrifugal force and adhesion. The disadvantage is that the rotating wet annular denuder contains a relatively large amount of liquid (about 15 mL), reducing the detection limit of determined compounds in the air (Večeřa et al., 2011).

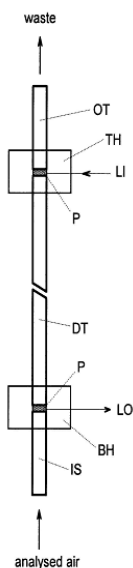


Figure 1: Wet Effluent Diffusion Denuder (WEDD): DT (denuder tube), IS (input of analysed air), OT (outlet tube), P (porous O-ring from polytetrafluorethan - PTFE), LI (input absorption liquid), LO (the output of the absorbing liquid), TH (upper ring), BH (lower ring).

Aerodispersing enrichment unit (AEU) is an enrichment device (Figure 2) with direct contact to the absorbing fluid and the analysed air. This device operates on the principle of equilibrial accumulation of pollutants from the gas phase using a polydispersed aerosol. The polluted air is sucked by a tube in which a stainless steel capillaries that supply absorption fluid are located. Using ejection effect of the air, the sorption liquid is dispersed as an aerosol. Polydispersed aerosol creates a narrow beam that is condensed in another part of the AEU due to quasi adiabatic expansion and clash with a sloping barrier. Sampling procedure enables automatic measurements (Večeřa et al., 2011).

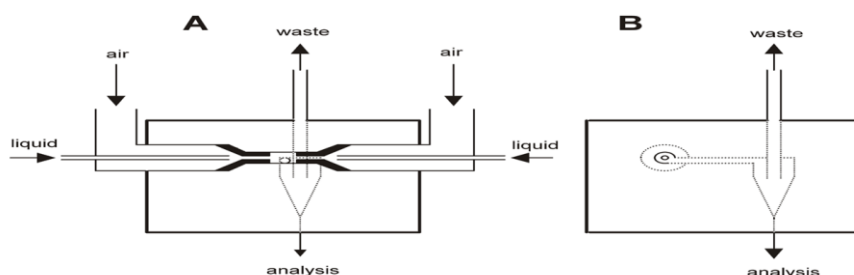


Figure 2: The proposed construction of two-lane AEU: (A) Front view; (B) Side view.

2.1 Sampling of gaseous substances

The most frequent sampling of gaseous substances is obtaining samples of air contaminated by unknown chemical as vapour or aerosol. There can also be obtained a sample of concentrated gas. These methods of sampling are extraordinary in practice. Generally, gas sampling is performed:

1. outdoors at the place with the highest concentration of DC, 20–30 cm above the ground,
2. indoors at the place with the highest concentration of DC, 1–105 m above the ground and at least 1 m from walls.

2.2 Sampling vapour or aerosol samples of explosives using a portable continuous aerosol concentrator

Portable continuous aerosol concentrator (PCAC) is a special sampling device working as aerodisperse enrichment unit (AEU) (Mikuška and Večeřa, 2005). Sucked pollutants are concentrated into the adsorbing liquid, which is collected into vial. Concentrator consists of:

- AEU,
- Pumps for air,

- Electronic components,
- Microfluidic elements allowing to set the amount of liquid entering the PCAC,
- Components and elements for controlling the amount of intake air,
- Electronic components for setting the operating time,
- Energy sources (Ni-Cd battery),
- Electronics used to recharge the battery from the electricity network.

All the above components are easily integrated into a portable box (see Figure 3).



Figure 3: Portable continuous aerosol concentrator (PCAC)

Available literature suggests that up until now there has been no known device that would work on the principle of AEU and which could be used for semi-continuous concentration of samples from the atmosphere. Practical application of PCAC allows air sampling and accumulation of organic and inorganic substances in the contaminated air. PCAC can be used for sampling and determining not only explosives, volatiles (VOCs) and semi volatile organic compounds (SVOCs), but also solids with a relatively low vapour pressure in the aerosol (Kellner and Večeřa, 2011). This concentrator is usable for measurement of VOCs and SVOCs, while water or n-heptane is used as an absorption liquid (Sklenská et al., 2002).

2.3 Description of the experiment

The concentration of DMNB (2,3-dimethyl-2,3-dinitrobutan, CAS 3964-18-9) in the range from 96 ppb to 23 ppm was successively prepared to a 5 L Flex film bag with the polypropylene (PP) fitting. DMNB was selected for the analysis as a marker with sufficient vapour pressure, which allows detection when mixed with explosives. The additive does not affect any of the properties of the explosive, which is a further big advantage. This material was consequently sampled from the bag into the PCAC that utilized heptane for the sorption. In all cases, 1 L of air was sucked at a flow rate of 0.5 L per minute. The determination was carried out on the original analyser of explosives developed in the framework of defensive research: PRINCIP OVUOFEM200904 (Večeřa et al., 2011).

3. Discussion

3.1 Outputs from the experiment

Simultaneous capture of gases, aerosols and ultrafine particles in particular using PCAC, enables highly sensitive determination of not only explosives, but also VOCs and SVOCs from the air. This method eliminates the disadvantages of other methods. It was necessary to supplement the acquired results with a measurement of the distribution of aerosol particles, preferably using SMPS devices to complement the experiment and obtain all relevant information. This measurement is described in the following example of our study.

3.2 Measurements of the distribution of ultrafine aerosol particles

Aerosol spectrometer SMPS (Model 3936L72, TSI) was used for the measurement. The particles were measured in the size range from 10 nm to 500 nm with a resolution of 64 channels per decade. In all cases, measurements were performed in a closed military workplace (see Figure 4). Five samples of air were analysed immediately in a row (time of analysis per sample was about 5 minutes, total measurement time was therefore approximately 25 minutes). All doors and windows in the room were closed during measurement. The signal from the device SMPS was evaluated by software Aerosol Instrument Manager (TSI, 2010), which allows to export values of normalized numerical concentration of particles (NC_i) in the analysed air sample for each channel. For the purpose of further calculations, the numerical particle concentrations measured in individual channels in 5 consecutive measurements were averaged for each channel. Further, the total particle number concentration (C_N) and a median particle diameter (M_D) were calculated. Based on the assumption of

a spherical shape of the particles, the total particle surface (SA), total particle volume (V) and a specific surface area (SSA) were calculated, where SSA equals share of SA divided by V. Furthermore, on the basis of the measured data mass concentration (C_M) of the particles and the specific surface energy (SSE) were estimated, where SSE equals the surface tension of water (σ) multiplied by the specific surface area (SSA).

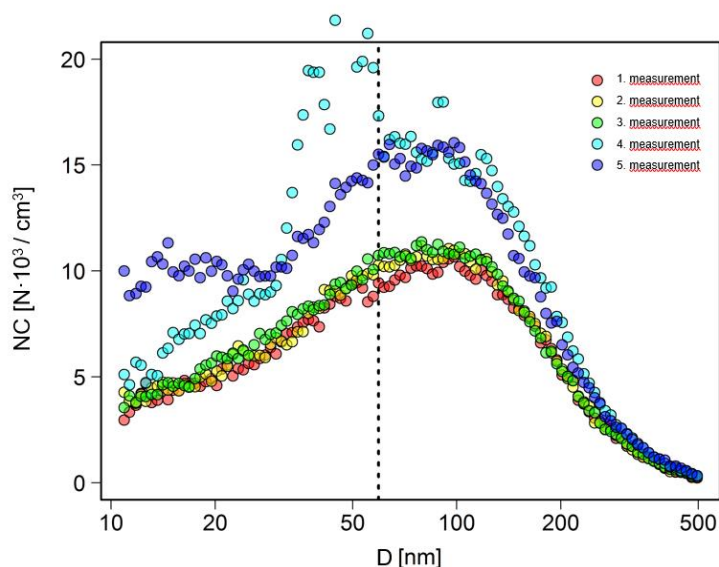


Figure 4: Measurement of a particle size distribution

Table 1: Comparison of average values for ultrafine particles from 10 nm to 500 nm on the workplace of the Armed Forces

	M_D [nm]	C_N [N.cm ⁻³]	C_M [μg.m ⁻³]	SA [μm ² .cm ⁻³]	V [μm ³ .cm ⁻³]	SSA [μm ⁻¹]	SSE [J.cm ⁻³]
10–100 nm	47	10505	1,59	91,92	1,06	86,51	6,3
100–500 nm	169	4277	25,9	445,35	17,26	25,8	1,88

*An error associated with the reproducibility data of the replicates occurred within the measurement. The error is the evidence of the magnitude of random error sources in the experiments.

Based on acquired results and error that occurred in the data reproducibility of the replicates, the test of long-term stability of SMPS measurement was performed. The testing evaluated a continuous generation of PbO nanoparticles (*in situ*) in a hot wall tube flow reactor. The long-term stability of generated PbO nanoparticles (NPs) was high. The relative standard deviations in median particle diameter (*i.e.*, 25.8 nm) and total particle concentration (*i.e.*, 1.23×10^6 particles.cm⁻³) were 3.9% and 3.1%, respectively. These values indicate that both the generation of NPs and the measurement of size distribution using the SMPS were very reproducible. The error that occurred can be assigned to actual situation of measurement of surrounding environment in real conditions.

3.3 The conclusions of the experiment

Comparing the measured values for nanoparticles of 10 nm to 100 nm and for particles of 100 to 500 nm, it was found that nanoparticles formed 71% of the total number of particles, but only 5.8% by weight concentration. Specific surface area (SSA) of acquired values was $86.51 \mu\text{m}^{-1}$ for the nanoparticles, but only $25.8 \mu\text{m}^{-1}$ for particles bigger than 100 nm. Specific surface energy (SSE) value was estimated at 6.3 J.cm^{-3} for nanoparticles, while only 1.88 J.cm^{-3} for particles of 100 nm to 500 nm.

4. Conclusion

During the industrial revolution, production of anthropogenic particles emitted into the atmosphere dramatically increased. Adverse impacts of small particles on human health has led to aimed regulation of their production. Nanoparticles and particles smaller than $1 \mu\text{m}$ are subject to Brownian motion induced by thermal motion of the air molecules. They do not drop on the ground and easily reach the pulmonary alveoli. Ultrafine

nanoparticles (1–100 nm) are nanoparticles that are close to the size of air molecules. Such substances can pass through the cell membrane and get into the blood, where they can threaten other organs. These aerosols are carcinogenic and the most dangerous form of air pollution, which causes oxidative stress. Scientific literature suggests that there is no safe amount of particles in the ambient air. The experiment described in this study evaluated the amount of nanoparticles in the air in a closed building of a selected military workplace. Results stated in the contribution suggest that the total particle number concentration was 10505 N.cm^{-3} for particles in size range from 10–100 nm and 4277 N.cm^{-3} for particles in size range from 100–500 nm. It is evident that the amount of smaller particles (10–100 nm) exceeds the number of larger particles (10–500 nm) more than twice. The rate for specific surface area and specific surface energy was even more than three times higher for smaller particles than for larger particles (SSA for the particles within 10–100 nm size was $86,51 \mu\text{m}^{-1}$ and within 100–500 nm $25,8 \mu\text{m}^{-1}$; SSE for 10–100 nm size of particles was $6,3 \text{ J.cm}^{-3}$ and for 100–500 nm $1,88 \text{ J.cm}^{-3}$). Such great amounts of fine particles in the air of military workplace may pose a health risk for soldiers present in such places for a long time.

The study was dedicated to the fundamental problem - sampling substances from the air. A number of methods use air sampling, but none of them has reproducible determination of all of these forms. The study presents a unique equipment - PCAC that eliminates these drawbacks and enables a rapid, reproducible and reliable collection of air samples. A great advantage is that it is a portable device enabling multiple repetition of the experiment. The second part was devoted to the issue of aerosols with an emphasis on ultrafine aerosols - nanoparticles. The findings are illustrated and evaluated in Table 1. Analysis of air using the SMPS devices and PCAC allows sampling aerosol within predetermined sizes of aerosol particles.

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