PHYSICAL CHEMICAL CHARACTERISTICS OF POWER PLANT EMISSIONS AND THEIR IMPACT ON HUMAN HEALTH

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S-au studiat pulberile generate la locul de muncă în termocentrale, cu referire specială la termocentrala de la Mintia - Deva. În scopul determinării compoziției pulberilor, s-a folosit analiza chimică structurală prin coroborarea datelor de analiză elementală obținute prin două metode: spectrometria de absorbție atomică şi analiza SEM-EDAX. Pulberile colectate de la diferite locații din termocentrală conțin peste 25% SiO2, 4% Al2O3, 10%Fe2O3. Impactul acestor particule asupra sănătății angajaților la aceste locuri de muncă diferite a fost evaluat prin teste specifice biochimice şi hematologice. Nivelul de citokin a fost propus ca un indicator adecvat pentru procesele inflamatorii asociate cu expunerea la noxe profesionale.

Workplace dusts generated in power plants, with particular reference to thermal power of Mintia - Deva have been studied. In order to determine the chemical composition of powder structural analysis was used by corroborating data obtained by elemental analysis performed by two methods: atomic absorption spectrometry and SEM-EDAX. Dust collected from various locations in power plant contained more than 25% SiO2, 4% Al2O3 10% Fe2O3. The impact of these particles on health workers in these different workplaces was assessed by specific biochemical and hematological tests. The level of cytokines was proposed as an indicator for the inflammatory processes associated with exposure to occupational hazards.

Keywords: dust, workplace health conditions, crystalline oxide noxes, power plant emissions, occupational exposure

1. Introduction

When examining an industrial enterprise from the toxicological point of view the workplaces supposed to be included within special conditions should be

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identified, while the determination of the occupational noxes should be made only based on the study of the technological process. This is referring to the detailed knowledge of the raw materials and materials, finished and intermediary products, equipment and technological process, operation of the respective equipment and tasks of the persons exposed. The noxes to be determined will be established taking into account that they can be generated from various chemical sources participating in the investigated process.

Analysis of the health conditions of employers exposed to noxes is essential in order to establish the appropriate measures need for preventing the personnel exposure to occupational noxes.

For the identification of noxes a series of physical-chemical properties should be taken into account, such as: the state of aggregation (vapours, gas or suspended matter, aerosols or dust), boiling point, vapour pressure, solubility, since knowledge of these parameters determines the working methods to be used when comply with European regulations [1].

When several noxes are simultaneously present in the same workplace, after the identification of such noxes, a classification and hierarchy of them should be made while taking into account their cumulated and synergistic action upon the human organism, establishing thus the level of risk on the personnel health [2-5].

The toxicity of the environmental particles has received significant attention along the time. The industrial ambient air monitoring collected key data of existing aerosol composition and structure in the workplace, their particulate matter (PM), size distribution and morphology that may be related to toxicological studies [6-8].

In this paper a special attention was paid to dust generated from the process of a power plant, with particular reference to Mintia – Deva power plant [9].

2. Experimental

The powders subjected to physical chemical analysis in this work have been sampled from three locations selected along the technologic process of Mintia – Deva power plant, particularly from the coal section, considered as having the highest hazardous impact on worker health. Coal is transported by conveying belt 1 (sample 1) to the coal storehouse in the breaking section (sample 2). In this place the coal is chopped, and then it is sent to the coal bunker with another conveying belt 2 (sample 3). From the bunker, the coal is then sent to power plant boiler.

Analysis of chemical-oxide powder composition of the atmosphere ELECTROCENTRALE DEVA work places was done according to RENAR accredited procedure PO-SME-10: “Analysis of the chemical-oxide deposits (Fe_2O_3, SiO_2, Al_2O_3, CaO, MgO, CuO, SO_4^{2-}, Na_2O, V_2O_3, NiO, ZnO, K_2O)”.

Sample preparation for chemical analysis was carried out by decomposition in a microwave digestion system - MILSTONE and metal composition analysis was performed on an atomic absorption spectrometer Thermo Scientific M-Series SOLAAR flame, graphite furnace and hydride generator.

The oxide composition of powders was confirmed by the elemental qualitative and quantitative analysis using an electronic microscop Philips XL 30 ESEM TMP, with 3.5 nm resolution and an acceleration tension of electron beam of 30 kV. The analysis of chemical composition was achieved by an energy dispersive X-ray spectrometer EDS, EDAX with resolution of 128 eV. The acquision time of data was established at minimum 35 Lsec and the results have been reported in mass and atomic percents.

Evaluation of toxicologic effect caused by nanoparticle powders has been made by investigation of cytokine profiles (IL-1β, IL-6, TNF-α) in serum, plasma or cell culture supernatants, by using multiplex platforms Luminex and xMAP ® 200 ™ (multi-analytic profiling). This system is able to perform simultaneous determination of multiple cytokines in small volumes of sample and to assess quickly the differences between various compounds. Indeed, Luminex ® 200 xMAP ™ has a potential of 100 cytokines simultaneous determinations, with the sample volume of 25-50 mL, being endowed with a more dynamic and wider field (~ 1-10000 pg / mL) than the classic method ELISA.

3. Results and discussion

The respiratory tract is the main route through which the dust enters the body, followed by ingestion. Deposition of dust in the pulmonary system varies considerably depending on the size of dust grain. The smaller it is, the deeper it penetrates and the hazardous effects on human health are more dangerous [10].

Recent studies show that ultrafine particles at nano-scale are more toxic than larger particles (micron) even if they have the same chemical composition and the same mass concentration. This is because smaller particles have a much higher specific area reported to mass, as compared to larger particles of the same mass. These nanoparticles can penetrate the respiratory tract and can be translocated from the lungs into the bloodstream, increasing the possibility that these nanoparticles not only to affect the lungs, but also to induce hemostatic disorders in lungs or in various other organs [11].

The workplaces under investigation for physical and chemical noxes (dust) are located inside the power plant, in a specific configuration of each operating section along technological process. These places have been selected from the work areas where the personnel serving equipment was the most exposed to the coal powders. [12]

In many cases great amounts of dust are generated whose concentrations overpass the admissible concentration established by the standards in force.

Concerning the oxidic composition of the powders collected from the three work places selected for this analysis, Table 1 shows the mass concentration of representative constituents.

Table 1

Mass concentration [%] of the powders collected from power plant of Deva-Romania

Compound	Sample 1	Sample 2	Sample 3
Loss on ignition at 180 ^oC	-	-	-
Loss on ignition at 500 ^oC	42.052	43.198	43.135
Loss on ignition at 850 ^oC	2.984	2.747	2.715
Loss on ignition at 950 ^oC	0.276	0.326	0.368
Silica	29.542	28.400	28.668
Sulfates	2.302	2.094	1.957
Fe_2O_3	3.685	4.444	4.336
Al_2O_3	9.590	2.862	9.086
Lime - CaO	1.725	2.434	2.729
Magnesia	1.153	1.976	2.144
Total vanadium expressed asV_2O_3	0.016	0.017	0.018
Nickel oxide	0.007	0.007	0.049
Copper oxide	0.017	0.015	0.019
Zinc oxide	0.011	0.011	0.011
Manganese oxide	0.021	0.020	0.026
Cadmium oxide	$11 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$2 \cdot 10^{-5}$
Massicot	0.008	0.006	0.008
Total chromium expressed as Cr_2O_3	0.016	0.016	0.093
Mercuric oxide	$<1.8 \cdot 10^{-5}$	$<1.8 \cdot 10^{-5}$	$<1.8 \cdot 10^{-5}$
Arsenic oxide	$2.9 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$
Sodium oxide	0.131	0.108	0.198
Potassium oxide	2.302	0.694	1.222

One can notice that the first 6 oxide compounds have a concentration higher than 1%. Moreover, it is noteworthy to mention that SiO_2 is predominant, being over 25%. The other significant constituents are Fe_2O_3 > 4%, Al_2O_3 >2%.

The same samples have been examined by SEM-EDAX elemental analysis (figures 1-3).

All the three samples contain as main elements: Ti, Ca, Ag, Fe, Al, Si, Pb, and K, and the highest peak is for Si from silica, which is in agreement with the elemental analysis data presented in table 1 obtained by AAS. Moreover, these major constituents might be responsible for the hazardous effects caused by these powders on worker health.

Concerning the possible impacts on human health and the environment there are many concerns that can arise when the smaller constituents of materials are brought down to the nanoscale.

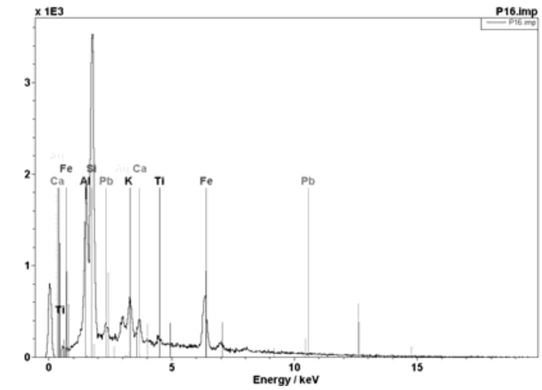

Fig. 1. EDAX spectrum of sample 1 - conveying belt 1

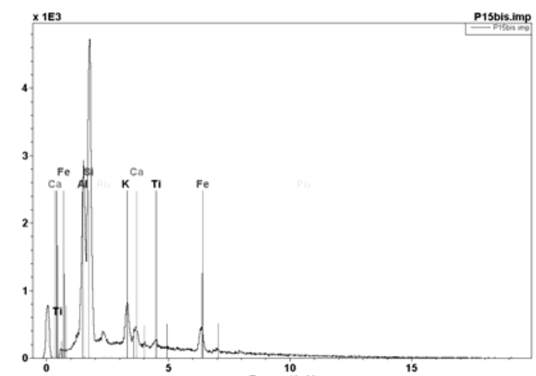

Fig. 2 EDAX spectrum of sample 2 - breaking section

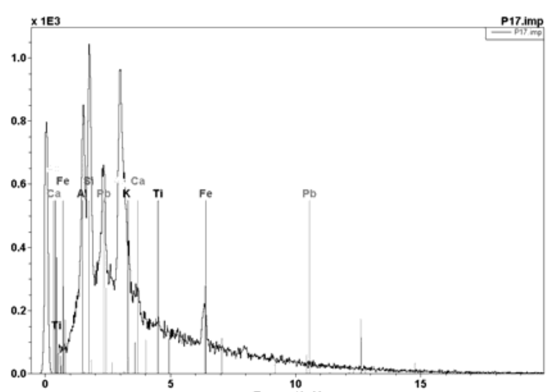

Fig. 3. EDAX spectrum of sample 3 – conveying belt 2

Although these impacts may not be different from those that can be caused by chemicals, it is not possible today to anticipate the impacts based solely on the chemical composition as such.

In order to assess the impact of powders on emloyers health three target groups have been established: the first group is formed from persons having around 10 years of work experience within the power plant (E10), the second group has around 20 years experience (E20), while the control group consisted in healthy subjects (nonsmokers).

As main indicator to assess the differences between various groups of subjects exposed to health hazards has been chosen the effect of modulation of serum cytokine profile correlated with biochemical and hematological parameters.

It should be mentioned that it is for the first time in Romania when this approach based on the evaluation of cytokine profile is applied in occupational exposure, through a modern technology platform using multiplex Luminex ® 200 xMAP ™ (multi-analytic profiling).

The possibility to use small volumes of sample allowed the comparison of these data with the behavior of peripheral blood cells from these subjects in cell cultures - *in vitro*, which has completed the information on immune status, immune defense capacity development or inflammatory processes associated with pathologies caused by exposure to hazards.

The reason to use the cytokine level as indicator on human risk is that they are produced by epithelial cells mesenchimal that amplifies the inflammatory response in lung and other organs. Indeed, these cytokines are produced in "cascade" in which the initial cytokine signals are amplified many times by target cells, epithelial cells, fibroblasts and endothelial cells. Cytokines function in networks in which feedbacks occur in many ways that coordinates and regulates cytokines and cell responses.

Now it is recognized that there is a complex balance between pro-inflammatory and anti-inflammatory cytokines, and "cytokine balance" is a key concept in understanding the activity of cytokines in biological fluids.

Appreciable increase of IL-1β interleukins in the groups exposed to hazards (table 2) may suggest increased susceptibility to hazards of this cytokine level, its modulation depending on exposure time.

IL-1β and IL-6 pro-inflammatory cytokines considered as markers of installation and development of diseases mediated by these mechanisms have shown a significant increase compared to control, but also a significant increase in the prolonged exposure group E20 compared to E10 group. Evolution of TNF-α in moderate exposure to hazards can be attributed to the fact that this cytokine level is increased early in response to toxic agents and is stabilized at high levels, thus stimulating other processes involved in inflammatory diseases.

Therefore, the level of inflammatory cytokines indicates the development of pulmonary pathologies and possibly of other organs in persons exposed to powder hazards, with increased pathology in chronic exposure.

Table 2

Levels of inflammatory cytokine in serum for target groups

Crt. No.	ID*	Age (years)	Work experience	IL-1β pg/mL	TNF-α pg/mL	IL-6 pg/mL
C	**m±SD**			**0.75±0.651**	**7.43±2.622**	**0.69±0.477**
1	P A	27	9	4.06	6.00	2.65
2	O A	29	10	2.94	10.60	2.41
3	C A	30	9	3.57	10.66	1.06
4	L M	36	14	3.08	7.42	1.06
5	M M	50	5	5.87	7.42	1.02
E10	**m±SD**			**3.90±1.187**	**8.42±2.09**	**1.64±0.816**
				$p>0.05$	$p>0.05$	$p>0.05$
6	C D	46	17	17.08	6.50	8.37
7	B B	41	21	11.97	10.18	4.24
8	C D	47	19	12.91	17.56	5.76
9	M V	51	19	19.48	10.68	7.90
10	M A	44	20	13.57	7.67	4.33
E20	**m±SD**			**15.00±3.163**	**10.52±4.299**	**6.12±1.944**
				$p^{**}<0.01$	$p^{**}<0.01$	$p^{**}<0.01$

TNF-α - tumor necrosis factor; IL-1β, IL-6 - interleukines
C – control, group of unexposed persons (healthy)
E10 - group of people exposed to hazards for cca. 10 years
E20 - group of people exposed to hazards for cca. 20 years
*ID – subject identitity

One of the most efficient solution aims at combating the scattering of the powders in the powder generation places by encapsulation of the powder generating equipment and diminution of the air pressure inside. Another solution was dilution of the powder concentrations *via* ventilation in the workplace by introduction of the conditioned air, using both general and local exhaust, and natural ventilation as well. A significant improvement of work conditions has been obtained by air humidifying. Indeed, by agglomeration of dust particles, their weight increases, thus facilitating the sedimentation on soil. This is completed by maintaining continuous cleanness by using a mobile vacuum cleaner.

4. Conclusion

The powders collected in three sites of Deva power plant, the coal section, contain various oxidic components, among them the major contribution having SiO_2 (> 25%), Fe_2O_3 (> 4%), Al_2O_3 (>10%). Chemical analysis carried out by AAS technique has been corroborated with elemental analysis made by SEM-EDAX technique, which confirmed the content of several elements like Ti, Ca, Ag, Fe, Al, Si, Pb, and K, with the highest contribution of Si in silica. Therefore this constituent seems to be responsible for the hazardous effect on workers exposed to the powders present in this atmosphere.

The impact of these particles on employer health at various workplaces has been evaluated by specific biochemical and haematological tests, the cytokine level being proposed as an appropriate indicator for the inflammatory process associated with the exposure to occupational noxes.

The implementation of a risk management program in workplaces with exposure to powders, including nanosized materials could contribute to minimize the potential health risk for exposure to such materials.

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