Morphological and Spectral Analysis of Nano-and Microparticles in Industrial Fume in the Electroplating Workshop

K Yu Kirichenko¹, I A Vakhniuk¹, D Yu Kosyanov¹, A S Kholodov¹, K S Golokhvat¹
¹Far Eastern Federal University, 8 Sukhanova Street, Vladivostok 690950, Russian Federation

E-mail address: Kirichenko2012@gmail.com

Abstract. The paper presents the results of chemical analysis of industrial fume samples collected in electroplating workshop at aluminum and non-ferrous metals processing lines using basic electrochemical processes. Using electron microscopy, images of production induced solid particles were obtained and morphological analysis of the surface of airborne particles was carried out.

1. Introduction

Despite current trends and toughening environmental legislation aimed at implementing environmentally friendly technologies in production, electrochemical processes are still used for applying protective coatings in the field of processing metal parts. Given the increased risk of particulate matter emissions into the atmosphere [1] and discharges of electrolyte solutions, electroplating urgently needs to switch to alternative “dry” coating processes, such as physical vapor deposition (PVD) [2], diffusion coatings with zinc and chromium, or microarc oxidation. These processes exclude the use of concentrated solutions containing heavy metal ions.

In the field of research, more attention was paid to the development of effective treatment facilities, the use of new wear-resistant materials to reduce wastewater pollution. [3, 4]. The study of airborne particulates in the air of working area, including nano- and micro-sized particulate matter in workshops and the adjacent territory, is given less importance, despite the possibility of their spread far beyond the sanitary protection zones of industrial enterprises [5]. These particles produce a significant effect on human health in industrial centers [6]. Late assessment of significance and danger of nano-technological contamination can reduce socio-economic indicators and the level of public health [7]. Industrial fume resulting from electroplating coating processes, as a rule, contains high-hazard substances based on heavy metals (Ni, Zn, Cu, Cr, etc.) [8, 9]. In particular, compounds of nickel (sulfate and chloride) and hexavalent chromium (chromium trioxide) can cause serious health consequences, including cancer, asthma, and dermatitis [10, 11].

The solution to the problem of reducing the negative impact of emissions is possible only after studying the characteristics of industrial aerosol particulates generated in an electroplating workshop. This paper deals with the analysis of the state of air environment inside an electroplating workshop and a comprehensive study of morphometric parameters and chemical structure of nano- and
microparticles formed at enterprises that use electroplating baths and apply basic electrochemical processes, in the context of monitoring atmospheric pollution with toxic substances of man-made origin.

2. Experimental
The sampling procedure was as follows: 2.7 liter sterile plastic containers with distilled water were placed on the floor of the workshop during its operation (Figure 1). Before the experiment the containers were thoroughly washed: 1 time with running water, 2 times with distilled water. After that the containers were filled to 1/3 of the total volume (600-800 ml) with distilled water obtained on the DE-4-02-EMO water distillator (Electromedoborudovanie, St. Petersburg, Russia). The still bath name (process), date and time were recorded for each sample.

![Figure 1. Plastic sampling containers.](image)

The experiment duration was 8 hours, equal to a shift in the workshop. The containers were placed near still baths and opened at 8:00 with the beginning of the work shift. At the end of the work shift at 5:00 pm, the containers were tightly closed, marked and transported to the laboratory for further research. Then the samples were dried in a TS-1/20 thermostat (Russia) for 24 hours at 40 °C. After the distilled water completely dried in the sampling containers, a sediment of solid particles of electroplating origin was sprayed onto pieces of double-sided carbon-containing adhesive tape, which were attached to aluminum cylinders for further research under a scanning electron microscope. A total of 10 were taken. (Table 1).

Table 1. Sampling for measurement of particle size distribution.

| №  | Sample point                | Electrolyte composition         |
|----|-----------------------------|---------------------------------|
| 1  | Aluminum cleaning           | HNO₃                            |
| 2  | Aluminum etching            | NaOH                            |
| 3  | Sulfuric acid anodizing     | H₂SO₄                           |
| 4  | Aluminum degreasing         | Na₂CO₃; Na₃PO₄                   |
| 5  | Chemical degreasing         | Detergent                       |
| 6  | Electrolytic degreasing     | Na₂CO₃; Na₃PO₄                   |
| 7  | Nonferrous metals etching   | HNO₃; H₂SO₄; HCl                |
| 8  | Chromium plating            | H₂CrO₄; H₂SO₄                   |
| 9  | Nickel plating              | NiSO₄; MgSO₄; Na₂SO₄; NaCl; H₃BO₃ |
| 10 | Chemical nickel plating     | NiSO₄                            |
The surface morphology of particulate matter was studied using scanning electron microscopy (Hitachi S3400N). Elemental analysis of the selected areas was carried out by energy dispersive X-ray spectroscopy with an electronic detector (ThermoScientific) at accelerating voltage of 20 KeV.

3. Results and discussion

The photographs of nano- and microparticles of industrial fumes collected in electroplating workshop are presented below (Fig. 2, Fig. 3, Fig. 4, Fig. 5).

Particles collected from samples No. 1 and No. 3 have similar morphological properties, they are porous agglomerates of primary particles.

![Electron microscope study of sample No. 1.](image)

Sample No. 2 (Fig. 3) includes spherical nanoparticles and acute-angle needle-shaped nanoparticles that have enhanced cytotoxic properties. When these particles enter the body through the respiratory tract, they pose the greatest threat to human internal organs. The elemental content of industrial fume particles is traditionally heterogeneous. In the studied samples, particles consisting of silicon, sodium, and chlorine oxides were detected most commonly. Nano- and submicron particles enriched with silicon are of spherical morphology. Silicon compounds (aluminum oxide and silicates) are formed when silicon is etched with alkali from aluminum alloys, where it is one of the basic additives (Fig. 1). In this sample, collected near the etching bath for aluminum parts, the content of Na was from 41% to 56%, and the content of Si was at 10%.

Sample No. 4 – individual bright shapeless inclusions with increased aluminum content were found during the analysis of chemical composition of particle surface (Fig. 5). In this sample, taken near the aluminum degreasing bath, aluminum oxides prevail, the content of the metal itself varying from 5% to 15%. This fact is due to the evaporation of the processed aluminum parts (aluminum preparation line). The presence of sodium in particles released during aluminum degreasing is explained by the composition of electrolyte, similar to aluminum etching process. The release of phosphorus compounds outside the bath is intensified by rapid aluminum degreasing process (CO₂ release during electrolysis of a Na₂CO₃ solution at 60-70 °C) (Fig. 5 c). It is known that such substances as white clay, corundum, tripolite (the basis of polishing tripoli paste) are additional additives for degreasing (cleaning) of soft metals. This may explain the presence of aluminum in the particle images after the degreasing process.
Figure 3. Electron microscope study of sample No. 2.
Figure 4. Electron microscope study of sample No. 3.

Figure 5. Electron microscope study of sample No. 4.
Sample No. 5 – despite the fact that this sample was taken near the electroplating bath for chemical degreasing of non-ferrous metal parts (and not on the aluminum preparation line), the maximum aluminum content registered was 25% (Fig. 6). It should also be noted that the content of chlorine was from 2% to 7%.

![Sample No. 5 - Electron microscope study of sample No. 5 (line 2).](image)

Sample No. 6 – in the sample taken near electrolytic degreasing bath, sulfur oxides dominated, reaching 30%. The content copper and zinc were at 15% and 5%, respectively.
Sample No. 7 – at the electroplating bath for etching non-ferrous metals, the sulfur content prevailed reaching 15% -25% and the content of sodium was 25%, similar to that in sample No. 6. Isometric fine particles with loose surface resulting from etching of non-ferrous metals are metal salts (nitrates, sulfates) (Fig. 8).
Sample No. 8, taken near the chromium plating bath (protective coatings line), has the richest elemental composition. The sample contained silicon – 2-27%, aluminum – 2-13%, iron – 1-23%, zinc – 2% and other inclusions (magnesium, molybdenum, titanium, chlorine and potassium).

Figure 8. Electron microscope study of sample No. 7 (line 2).
The sources of rich elemental composition of airborne particles released during chromium plating and nickel plating are the electrolyte composition and the surface of processed parts. In particular, their chemical interaction at the initial moments of electrolysis leads to the formation of metal-containing APs (with Al, Fe, Zn, Cu, Cr).

Figure 9. Electron microscope study of sample No. 8 (line 3).
The heterogeneity of the chemical composition along with the chemical composition of the electrolyte is predetermined by the technological features of the electrochemical processes, such as the duration of processing of a part and the temperature regime of electrolyte. In addition, heterogeneous chemical composition and the change in particle size distribution are due to physicochemical transformations of primary particles during their propagation in air [13].

4. Conclusions
It is known that harmful industrial particles enter the organisms of electroplaters not only through the respiratory tract, but also through skin, ears, eyes and other unprotected parts of the body [14]. Therefore, it is imperative that workers use personal protective equipment for eyes and breathing [15]. Workers in electroplating production need constant biomonitoring of blood and urine in order to assess and control general health risks based on warning reports.

Quantitative and mass concentrations of airborne particles inside the electroplating workshop were estimated. Despite the high content of airborne particles, the maximum permissible concentration was not exceeded. Most likely, handheld particle counter registered fumes formed during evaporation of the contents of electroplating baths.

The morphological structure of the surface of particles formed during various technological processes is non-uniform. Rounded particles, various agglomerates with complex geometric shapes, acute-angled particles that pose the greatest threat to human health were identified.

Chemical analysis of these particles showed the absolute predominance of non-ferrous metal oxides, the percentage of which varied depending on the type of electroplating process. Hazardous
substances (Zn and Mo) were identified, but their content did not exceed the maximum permissible concentrations.

Installing drip traps will help to avoid propagation of harmful particles into the working area, thereby reducing the negative impact on the workshop employees and employees of related professions. Minimizing the pollution of the working zone air with highly toxic substances generated by electroplating requires a comprehensive approach to mandatory modernization of ventilation systems, introduction of modern personal protective equipment, use of less concentrated electrolyte solutions, and gradual transition to environmentally friendly alternative processes for applying protective coatings to metal parts.

References
[1] Omelchenko E V, Trushkova E A, Sidelnikov M V, Pushenko S L, Staseva E V 2017 Algorithm Research Exposure Dust Emissions Enterprises of Building Production on the Environment IOP Conference Series: Earth and Environmental Science vol 50 Issue 1 10 012018 DOI: 10.1088/1755-1315/50/1/012018
[2] Navinšek B, Panjan P, Milošev I 1998 PVD coatings as an environmentally clean alternative to electroplating and electroless processes Surface and Coatings Technology vol 116-119 pp 476-487 Proceedings of the 1998 6th International Conference on Plasma Surface Engineering (PSE-98) Garmisch-Partenkirchen
[3] Dyachenko A V, Ilyin V I 2009 Development of technical solutions to reduce environmental pollution by electroplating Ecology of industrial production 3 pp 47-49
[4] Mavletov M N, Berezin N B, Yarullin A Z, Farrakhov G R, Nurullin A B 2017 The use of a circulation station for cleaning rinse water in electroplating workshops Bulletin of the Technological University vol 20 2 pp 51-53
[5] Golokhvast K S, Shvedova A A 2014 Galvanic Manufacturing in the cities of Russia: Potential source of ambient nanoparticles Plos One vol 9 Issue 10 e110573
[6] Oberdörster G A, Oberdörster E, Oberdörster J 2005 Nanotoxicology: An emerging discipline evolving from studies of ultrafine particles Environmental Health Perspectives vol 113 Issue 7 pp 823-839
[7] Drozd V A, Kholodov A S, Agoshkov A I, Petukhov V I, Blinovskaya Ya Yu, Lushpey V P, Vasyanovich Yu A, Solomenkiv S F, Fatkulin A A, Slesarenkov V V, Minaev A N, Gulkov A N, K S Golokhvatov 2016 Potential toxic risk from the nano- and microparticles in the atmospheric suspension of Russky Island (Vladivostok) Der Pharma Chemica 8(11) 231-235
[8] Silva J E, Paiva A P, Soares D, Labrincha A & Castro F 2005 Solvent extraction applied to the recovery of heavy metals from galvanic sludge J. Hazard. Mater. 120(1–3) 113–118
[9] Rossini G & Bernardes A M 2006 Galvanic sludge metals recovery by pyrometallurgical and hydrometallurgical treatment J. Hazard. Mater. 131(1–3) 210–216
[10] Beattie H, Keen C, Coldwell M, Tan E, Morton J, McAlinden J & Smith P 2017 The use of biomonitoring to assess exposure in the electroplating industry J. Expo. Sci. Environ. Epidemiol. 27(1) 47–55
[11] Pan C-H, Jeng H A & Lai C-H 2018 Biomarkers of oxidative stress in electroplating workers exposed to hexavalent chromium J. Exp. Sci. Environ. Epidemiol. 28(1) 76–83
[12] Baracchini E, Bianco C, Crosera M, Filone F L, Belluso E, Capella S, Maina G, Adami G Nano- and Submicron Particles Emission during Gas Tungsten Arc Welding (GTAW) of Steel: Differences between Automatic and Manual Process Aerosol and Air Quality Research vol 18 Issue 3 pp 579-589
[13] Song Guo, Min Hu, Misti L Zamora, Jianfei Peng, Dongjie Shang, Jing Zheng, Zhuofei Du, Zhijun Wu, Min Shao, Limin Zeng, Mario J Molina and Renyi Zhang 2014 Elucidating severe urban haze formation in China Proceedings of the National Academy of Sciences of the United States of America vol 111 Issue 49 pp 17373-17378
[14] Halliday-Bell J, Palmer K & Crane G 1997 Health and safety behaviour and compliance in
electroplating workshops *Occup. Med. (Lond)*. **47**(4) 237–240

[15] Beattie H, Keen C, Coldwell M, Tan E, Morton J, McAlinden J & Smith P 2017 The use of biomonitoring to assess exposure in the electroplating industry *J. Expo. Sci. Environ. Epidemiol.* **27**(1) 47–55

**Acknowledgements**

The authors would like to thank the staff of the Center for Collective Usage FEFU for providing research equipment.

The work was supported by the Grant of the President of the Russian Federation for young Russian PhDs (MK-2461.2019.5).