Study of Heavy Metals Toxicity Level in Workplace Atmosphere by Alternative Methods

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Abstract. Promoting safety and health at work, as part of the overall improvement of working conditions, is an important strategy, not only to ensure well-being of workers, but also to make a positive contribution to productivity. Health, safety and well-being of workers are therefore prerequisites for improving quality and productivity and are important for equitable and sustainable socio-economic development. Toxicological investigation of an industrial objective involves both knowledge of working conditions and the dynamic establishment of occupational pollutants in the workplace atmosphere, as well as bio-toxicological evaluation, being a synthetic representation of the aggressiveness of pollutants entering the body by various paths (respiratory, cutaneous, digestive, etc.) with reference, at the same time, to the adaptability of respective employees. Evaluation of the toxicological investigation has a role in following the evolution of working conditions and health of employees in time, potential technological changes with possible impact on employees’ health, as well as if new conditions occur, requiring the completion of previous toxicological investigations. Use of heavy metals in different industries has increased the quality of products from different production sectors but on the other hand also led to an increase in the toxicity of workplace atmosphere, which requires an assessment of the negative impact produced. The current paper aims at an alternative analysis of the determination of heavy metals content (Cu, Cd, Pb, Ni, Cr) in workplace atmosphere, using, on one hand, the method of spectroscopy of atomic emissions with inductively coupled plasma and, on the other hand, fluorescence with X rays. Following statistical processing of data gathered by the two alternative methods, the accuracy, reproducibility, relative standard deviation as well as the fidelity of methods expressed by the coefficient of variation will be established.

1. Introduction

Occupational exposure to chemical agents can be assessed by measuring the concentration of the toxic agent in the air of work areas and/or by measuring biological parameters in exposed personnel [1].

The investigation of working conditions includes several stages of study, namely: documentation (collecting data on the objective studied and technological processes taking place in that unit), identification of toxins found at a specific workplace (based on the study of technological process), taking samples from the workplace (from all places where operators find themselves during work), analytical determination of noxious substances by various methods such as the atomic emission spectrometric method with inductively coupled plasma, Energy Dispersive X-Ray Fluorescence) as well...
as interpretation of results (results obtained will be compared to the occupational exposure limit values for chemical agents provided by in force legislation) [2].

In order to understand the phenomenon of industrial toxicology in depth, it is necessary to showcase the concept of industrial (occupational) hygiene, materialized through science and engineering of preventing diseases caused by the environment in which workers work [3, 4]. It helps employers and employees understand risks in the workplace in order to improve working conditions and practices. Another term to be stated is "chemical agent" defined as any chemical element or compound, alone or in a mixture, in its natural state or manufactured, used or released, including as waste, from any activity, whether or not intentionally produced, whether or not it is placed on the market [5].

Because heavy metals (Cu, Cd, Pb, Ni, Cr) have negative effects on workers' health, they were chosen to be determined.

In order to assess heavy metal concentrations in workplace atmosphere, two methods of heavy metal measurement were used, namely inductively coupled plasma atomic emission spectrometry and X-ray fluorescence (XRF) analysis.

2. Measurement of heavy metals by inductively coupled plasma atomic emission spectrometry

ICP-OES has two parts: the ICP and the optical spectrometer. The ICP torch consists of 3 concentric quartz glass tubes. The output or "working" coil of the radio frequency (RF) generator surrounds part of this quartz lantern. Gaseous argon is usually used to create plasma. ICPs have two operating modes, called low plasma density capacitive mode (E) and high plasma density inductive mode (H), and the transition from heating mode E to H takes place by external inputs. [6] The torch is operated in H mode.

When the torch is turned on, an intense electromagnetic field is created in the coil by the high frequency radio signal flowing in the coil. This RF signal is created by the RF generator which is effectively a high-power radio transmitter that drives the "working coil" in the same way that a typical radio transmitter drives a transmitting antenna. Typical instruments run at either 27 or 40 MHz.

The argon gas flowing through the torch is ignited with a Tesla unit that creates a short discharge arc through the argon flux to initiate the ionization process. Once the plasma is "on", the Tesla unit is turned off. Argon gas is ionized in the intense electromagnetic field and flows in a certain symmetrical rotational pattern to the magnetic field of the RF coil. A stable, high-temperature plasma, of about 7000 K, is then generated as a result of inelastic collisions created between neutral argon atoms and charged particles.

A peristaltic pump delivers an aqueous or organic sample to an analytical nebulizer, where it is turned into mist and placed directly into the plasma flame. The sample immediately collides with the electrons and ions charged in the plasma and is itself divided into charged ions. The different molecules break into their respective atoms, which then lose electrons and recombine repeatedly in the plasma, emitting radiation at the characteristic wavelengths of the elements involved. In some models, a shear gas, usually nitrogen or dry compressed air, is used to "cut" the plasma at a specific point.

One or two transfer lenses are then used to focus the light emitted on a diffraction grating where it is separated into its component wavelengths in the optical spectrometer. In other models, the plasma directly affects an optical interface consisting of an orifice from which a constant flow of argon emerges, which deflects the plasma and ensures cooling while allowing light emitted from the plasma to enter the optical chamber. Other models use optical fibres to transmit some of the light into separate optical chambers. In the optical chamber(s), after the light is separated into its various wavelengths (colours), the light intensity is measured with a physically positioned photomultiplier tube or tubes to 'visualize' the specific wavelength (e) for each element line involved, or, in more modern units, the separate colours
fall on a series of semiconductor photodetectors, such as charge-coupled devices (CCDs). In units using these detector arrays, the intensities of all wavelengths (within the system range) can be measured simultaneously, allowing the instrument to perform analyses for each element to which the unit is sensitive, simultaneously. Thus, the samples can be analysed very quickly.

The intensity of each line is then compared with the previously measured intensities of the known element concentrations, and their concentrations are then calculated by interpolation along the calibration lines. In addition, the special software generally corrects the interference caused by the presence of different elements in a given sample matrix. Metal determinations were performed with the equipment shown in Figure 1.

![Optima 2100 DV inductive atomic emission spectrometer](image)

**Figure 1.** Optima 2100 DV inductive atomic emission spectrometer

### 3. Measurement of heavy metals by X-ray fluorescence (XRF)

The principle on which X-ray fluorescence (XRF) analysis is based is the electronic transition between two electronic layers of the atom. This transition can cause the emission of a photon whose energy is closely related to the energy difference between layers. Because each element has its own energy level configuration, it emits a unique set of X-rays, making it possible to identify it.

The fluorescence spectrum is presented as an alignment of the line. The energy or wavelength of the lines is determined by the energy difference between transition levels involved and identification of the chemical element. The intensity of lines is associated with concentration of the identified element. The XRF analysis system is considered to be a versatile tool because of its advantages, especially the fact that it is a non-destructive and fast analysis. It should be borne in mind that quantitative determinations are difficult to achieve because of intrinsic limitations.

The attenuation coefficient of materials is extremely high in energies of several tens of keV and, therefore, thickness of the analysed material is reduced to several tens of μm below the surface of the analysed layer. In addition, the X-ray detection rate depends not only on the abundance of corresponding elements, but also on the presence of all other components of the sample [7]. Therefore, in most cases of practical interest, the XRF analysis system can be considered as a qualitative or semi-quantitative analytical technique.

The analysis method is very applicable and is used along with other complementary methods of investigation. Certain biological samples are often unique and sometimes difficult to transport, so a
portable XRF detector system that allows in situ analysis is ideal for applications in research and conservation of aquatic ecosystems.

Figure 2. Hitachi X-MET8000 XRF Handheld Analyzer

Qualitative analysis is based on the position of fluorescence peaks in spectrum. This position depends on the energy of X-rays and therefore on the frequency of X-rays characteristic of elements in the sample, which is why, based on Moseley's law, the Z number of elements in the sample can be determined. The XRF wavelength and relative intensities for a given element are constant in a first approximation.

A large exploration area in XRF involves the use of light X-ray spectrum for qualitative analysis. Peaks of this radiation reveal the fine structure which is a direct indication of the electronic structure (chemical bond) around the emitting atom. Thus, change in the position of a peak represents a change of the intensity distribution or appearance of an additional peak and can be correlated with various chemical factors, such as the oxidation state, the coordination number and nature of the covalent bond. Quantitative analysis is performed by determining the intensity of characteristic radiation emitted by elements of the sample. This intensity is determined by the area of each line in the spectrum. At the same time, in case of a certain element in a homogeneous sample, it depends practically on the presence of all the elements in the sample.

In case of high-precision quantitative analysis, XRF spectrometers are calibrated using standards with known element concentrations, these standards being of the same type as the samples analyzed. For high concentration components, accuracy of the XRF technique has the same order of magnitude as the chemical analysis methods. The method is selective, showing very little spectral interference due to the relative simplicity of the X-ray spectrum. Another advantage would be that the method is non-destructive, no chemical preparation is required for solid samples, only grinding and pressing in the form of pills. Size and shape of particles are important because they determine the degree to which incident X-rays are absorbed or scattered. Metal determinations were performed with the equipment shown in Figure 2.
4. Results and discussions
Determinations were performed at an industrial unit whose object of activity is refining and processing heavy metals (Cu, Cd, Pb, Ni, Cr). Sampling was performed simultaneously for 8 hours, at a suction flow of 2.2 l/min, on microfiber glass filters.

In order to have certainty of results obtained by the two alternative methods, the following will present some performance criteria applied to results obtained from determinations [7, 8].

In order to verify the two alternative methods for determining heavy metals in workplace atmosphere, we will use certain benchmarks provided by the standard SR EN ISO / IEC 17025:2008 [9].

Comparative analysis consisted of results / statistical comparison between Inductively coupled plasma optical emission spectrometry (Optima 2100 DV) and X-ray fluorescence analyser X-MET8000.

Table 1 Shows the technical data entry for the two measuring instruments.

| No. | Data                  | Optima 2100 DV | X-MET8000  |
|-----|-----------------------|----------------|-------------|
| 1   | Equipment manufacturer| PerkinElmer, USA| Hitachi, Japan|
| 2   | Measuring:            | Concentration of Cu, Cd, Pb, Ni and Cr |
| 3   | Measuring method:     | Inductively coupled plasma optical emission spectrometry | Energy Dispersive X-Ray Fluorescence |
|     |                       | Cu: 0 – 100 [ppm] | Cu: 0 – 100 [ppm] |
|     |                       | Cd: 0 – 100 [ppm] | Cd: 0 – 100 [ppm] |
|     |                       | Pb: 0 – 100 [ppm] | Pb: 0 – 100 [ppm] |
|     |                       | Ni: 0 – 100 [ppm] | Ni: 0 – 100 [ppm] |
|     |                       | Cr: 0 – 100 [ppm] | Cr: 0 – 100 [ppm] |
| 4   | Measurement range:    | Cu: 0,01 [ppm]  | Cu: 0,05 [ppm] |
|     |                       | Cd: 0,01 [ppm]  | Cd: 0,05 [ppm] |
|     |                       | Pb: 0,01 [ppm]  | Pb: 0,05 [ppm] |
|     |                       | Ni: 0,01 [ppm]  | Ni: 0,05 [ppm] |
|     |                       | Cr: 0,01 [ppm]  | Cr: 0,05 [ppm] |
| 5   | Measurement precision:|                |             |
| 6   | Calibration Certificate| CE: xx-xxx/2020 | CE: xx-xxx/2020 |
| 7   | Matrix:               | Liquids / Solids |             |

Tests were carried out on five types of heavy metals by two operators with the two types of equipment. Tables 2 and 3 show the reference concentrations and values obtained by tests.

| OPERATOR 1 | Mean concentration value | Obtained concentration value (Optima 2100 DV) | Obtained concentration value (X-MET8000) |
|------------|---------------------------|-----------------------------------------------|----------------------------------------|
| Cu: 0,35 (ppm) | Cu: 0,33 (ppm)            | Cu: 0,34 (ppm)                                |
| Cd: 0,4 (ppm)  | Cd: 0,38 (ppm)            | Cd: 0,42 (ppm)                                |
| Pb: 0,25 (ppm) | Pb: 0,24 (ppm)            | Pb: 0,28 (ppm)                                |
| Ni: 0,35 (ppm) | Ni: 0,34 (ppm)            | Ni: 0,36 (ppm)                                |
| Cr: 0,6 (ppm)  | Cr: 0,62 (ppm)            | Cr: 0,64 (ppm)                                |
Table 3. The value of the concentrations obtained by the second operator

| OPERATOR 2 | Mean concentration value | Obtained concentration value (Optima 2100 DV) | Obtained concentration value (X-MET8000) |
|------------|--------------------------|-----------------------------------------------|----------------------------------------|
| Cu: 0,35 (ppm) | Cu: 0,34 (ppm) | Cu: 0,35 (ppm) |
| Cd: 0,4 (ppm)     | Cd: 0,39 (ppm) | Cd: 0,43 (ppm) |
| Pb: 0,25 (ppm)    | Pb: 0,25 (ppm) | Pb: 0,29 (ppm) |
| Ni: 0,35 (ppm)    | Ni: 0,35 (ppm) | Ni: 0,37 (ppm) |
| Cr: 0,6 (ppm)     | Cr: 0,64 (ppm) | Cr: 0,66 (ppm) |

Performance requirements analysis was determined [10] by calculating the standard deviation, the repeatability / reproducibility limit, the relative standard deviation under repeatability / reproducibility conditions, the fidelity and the measurement uncertainty, as follows:

Repeatability limit - the approximation between the results of successive measurements of the same measurement performed under the same measurement conditions (Table 4).

Table 4. Repeatability limit values

| Concentration | Optima 2100 DV | X-MET8000 |
|---------------|---------------|-----------|
| Cu: 0,35 (ppm) | 0,07          | 0,08      |
| Cd: 0,4 (ppm)  | 0,05          | 0,06      |
| Pb: 0,25 (ppm) | 0,06          | 0,07      |
| Ni: 0,35 (ppm) | 0,03          | 0,03      |
| Cr: 0,6 (ppm)  | 0,13          | 0,15      |

Conclusion: Performance requirement met.

Relative standard deviation under repeatability conditions - expressed as a percentage of the range covered during the test procedure (Table 5).

Table 5. Relative standard deviation under repeatability conditions

| Concentration | RSD, [%] |
|---------------|----------|
| Cu: 0,35 (ppm) | 7,49     |
| Cd: 0,4 (ppm)  | 4,94     |
| Pb: 0,25 (ppm) | 9,62     |
| Ni: 0,35 (ppm) | 3,29     |
| Cr: 0,6 (ppm)  | 7,64     |

Conclusion: Performance requirement met.

Reproducibility limit values from separate experimental studies are considered "proportional" if they are obtained according to the same reproducible experimental description. (Table 6)

Table 6. Reproducibility limit values

| Concentration | Reproducibility limit |
|---------------|-----------------------|
| Cu: 0,35 (ppm) | 0,07                  |
| Cd: 0,4 (ppm)  | 0,17                  |
| Pb: 0,25 (ppm) | 0,12                  |
| Ni: 0,35 (ppm) | 0,06                  |
| Cr: 0,6 (ppm)  | 0,06                  |
Conclusion: Performance requirement met.

Relative standard deviation in reproducibility conditions - expressed as a percentage of the range covered during the experimental approach (Table 7).

| Concentration | RSD (%) | RSD (%) |
|---------------|---------|---------|
| Cu: 0.35 (ppm) | 7.71    | 8.76    |
| Cd: 0.4 (ppm)  | 13.93   | 15.82   |
| Pb: 0.25 (ppm) | 15.15   | 17.21   |
| Ni: 0.35 (ppm) | 5.85    | 6.65    |
| Cr: 0.6 (ppm)  | 3.36    | 3.82    |

Conclusion: Performance requirement met.

Fidelity (accuracy) - expressed by the coefficient of variation (Table 8) calculated as a fraction of the standard deviation of obtained concentration values and reference concentration values.

| Reference concentration value | Variation coefficient [%] | Variation coefficient [%] |
|-------------------------------|---------------------------|---------------------------|
| Cu: 0.35 (ppm) | 0.06 | 0.07 |
| Cd: 0.4 (ppm)  | 0.04 | 0.14 |
| Pb: 0.25 (ppm) | 0.09 | 0.16 |
| Ni: 0.35 (ppm) | 0.03 | 0.06 |
| Cr: 0.6 (ppm)  | 0.07 | 0.03 |

Conclusion: The fidelity criterion is checked for Variation coefficient < 1%

Measurement uncertainty - the expression of the statistical dispersion of the values attributed to measured quantities [11].

| Reference concentration | Composed uncertainty | Extended uncertainty | Reference concentration | Composed uncertainty | Extended uncertainty |
|-------------------------|----------------------|----------------------|-------------------------|----------------------|----------------------|
| Cu: 0.35 (ppm) | 0.041 | 0.082 | Cu: 0.35 (ppm) | 0.049 | 0.098 |
| Cd: 0.4 (ppm)  | 0.047 | 0.095 | Cd: 0.4 (ppm)  | 0.060 | 0.121 |
| Pb: 0.25 (ppm) | 0.030 | 0.060 | Pb: 0.25 (ppm) | 0.040 | 0.081 |
| Ni: 0.35 (ppm) | 0.042 | 0.085 | Ni: 0.35 (ppm) | 0.052 | 0.104 |
| Cr: 0.6 (ppm)  | 0.077 | 0.155 | Cr: 0.6 (ppm)  | 0.092 | 0.184 |

Table 9 shows a higher accuracy of heavy metal determination method with the help of ICP-OEM.

5. Conclusions

In Romania, Law 319/2006 with subsequent amendments and completions establishes the general principles regarding prevention of occupational risks, the protection of workers' health and safety, the elimination of risk and injury factors as well as training of workers.

We decided to determine heavy metals (Cu, Cd, Pb, Ni, Cr) because in workplace atmosphere these toxins cause airway irritation, gastrointestinal irritation (Cu, Cr) and damage to the nervous system (Pb).
The two methods for determining metals in the workplace atmosphere are a viable alternative to the reference methods currently in use.

The advantage of using the ED XRF method lies in the short response time regarding metal concentrations in air, on the other hand the ICP-OES method of determination offers the advantage of a more accurate determination.

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