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k_0-INAA performance in the measurement of filters sampled in an industry with high loadings of metals

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ABSTRACT

Foundry industry has important environmental and occupational health impacts. More information is needed to properly assess occupational health risks presented by this industrial sector. This works aims at (1) characterizing the workers exposure to particulate matter in the foundry industry using k_0-Instrumental Neutron Activation Analysis (k_0-INAA) and Particle-Induced X-Ray Emission (PIXE) and (2) identifying some weakness of the k_0-INAA technique when high concentrations of particulate matter and metals are involved. Filters were collected in a foundry industry which processes Pb and were analysed by k_0-INAA and PIXE. In INAA, the incomplete deposition of gamma-rays in the germanium crystal due to Compton scattering elevated the spectra baseline, thus increased the background, and hindered the identification of some photopeaks. The problem was particularly important due to the high Sb contents existing in the sampled filters. The application of the Compton Suppression System for the analysis of these filters was successfully used in order to ascertain potential improvements on the detection limits for Zn and Fe. Results obtained showed that in this foundry industry workers were exposed to high concentrations of Pb, Sb, Fe, Sn, As, Ni, Br, Na and Cl.

1. Introduction

Workers in the foundry industry are exposed to numerous substances with known neurotoxicity, genotoxicity, carcinogenic, allergenic and immunological effects. The main health risk is associated with inhalation of particulate matter, which contains elevated levels of elements, such as Cd, Cr, Fe, Pb, Sb and Zn. There is a growing need to harmonize activities in the field of occupational health methodology and approaches to risk assessment in which direct monitoring can be used.

Despite the several decades of analytical research in outdoor air particulate matter characterization by k_0-INAA [1–5], the determination of the chemical composition of particles in the industrial environment is not a trivial task and faces difficulties in the analytical investigations due to the complex nature of the samples. The problem is particularly important because high loading of metals elevates the backgrounds which highly increase the detection limits for some elements that usually are easily determined by this technique (e.g. Zn and Fe).

2. Experimental

2.1. Description of the sampling equipment

Sampling was performed in a foundry workplace which processes lead. Particles were sampled during 1 h periods with four low-volume Gent samplers [6] working in parallel. These samplers were equipped with a PM_{10} pre-impactor stage and with a Stacked Filter Unit (SFU). The SFU carried, in two different stages, two 47 mm Nuclepore polycarbonate filters. Air was sampled at a rate of 15–16 l min^{-1}, which allowed the collection of particles with aerodynamic diameter (AD) between 2.5 and 10 μm in the first stage and particles with AD <2.5 μm in the second stage. During this sampling campaign 16 filters were collected.

2.2. Gravimetric and chemical analyses

The filter loads were measured by gravimetry in a controlled clean room (class 10,000). Nuclepore filters were weighted on a semi-micro balance. Filter mass before and after sampling was obtained as the average of three measurements, when observed variations were less than 5%.

Each filter was divided into four parts. For chemical identification, one quarter was analyzed by PIXE (for Al, Ca, Cl, Cu, K, Mn,

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Ni, Pb, Si, Ti and V quantification), another quarter by INAA (for As, Br, Cd, Cr, Fe, Na, Sb, Se, Sn and Zn quantification) and the remaining half of the filter was stored for future analysis.

PIXE [7] was carried out at a Van de Graaff accelerator, in vacuum and two X-ray spectra were taken for each of the samples; one with a 1.2 MeV proton beam and no absorber in front of the Si(Li) detector for low-energy X-ray elements and another with a 2.4 MeV proton beam and a 250 μm Mylar® filter to detect elements with atomic number higher than 20. The beam area at the target was 20 mm^2.

For INAA [8], the filter quarter was rolled up and put into a thin foil of aluminium and irradiated for 5 h at a thermal neutron flux of $1.03 \times 10^{13}\,cm^{-2}\,s^{-1}$ (f=103.4 ± 1.3; α= −0.035 ± 0.0001; T_n=330 K) in the Portuguese Research Reactor. After irradiation the sample was removed from the aluminium foil and transferred to a polyethylene container. For each irradiated sample, two gamma spectra were measured with a hyperpure germanium detector, one spectrum was measured 3 days after the irradiation and the other one after 4 weeks. The k_0-INAA method [9] was used and 0.1% Au–Al discs (Institute for Reference Materials and Measurements reference material 530) were co-irradiated as comparators. Measurements were also done 5 days after irradiation using Compton Suppression System (five Ortec NaI(Tl) crystals around and one Ortec crystal on top, with detector and electronics from Canberra). Compton-suppressed spectra were acquired simultaneously with the regular ones. Elemental masses were calculated using the relative method and the National Institute of Standards and Technology (NIST) standard 1633a-Coal Fly Ash, which was co-irradiated with the samples.

Blank Nuclepore filters were treated as regular samples. All measured species in the blank were very homogeneously distributed; therefore loaded filters concentrations were corrected by subtracting the filter blank contents.

3. Results

In order to perform the quality control of the k_0-INAA process, samples were irradiated with the NIST standard 1633a-Coal Fly Ash. Table 1 shows that, except for Sb, the results obtained for standards were in agreement within the certified values. For Sb, it was verified that the measured concentrations in the reference material depended on the Sb contents present in the samples, which were irradiated with the reference material: (1) the highest ratio measured/reference value (6.6) was observed when the reference material was irradiated with filters with highest Sb contents and (2) the lowest ratio (0.8) was registered when the reference material was irradiated with the blanks. These results showed that in the analysis of filters with high Sb loadings, an appropriate packaging should be applied in order to avoid contaminations. In the present study, contamination affected the quality control results and, consequently, it is expected that this was the reason for the Sb results of the filters to be biased.

Table 1
Certified and determined values for Coal Fly Ash standard reference material (SRM-1633a).

	Certified value (μg/g)	This work (μg/g) (n=4)
As	145 ± 15	140 ± 9
Cr	196 ± 6	190 ± 30
Fe	94,000 ± 1000	92,000 ± 8000
Na	1700 ± 100	2100 ± 490
Sb	6.8 ± 0.4	25 ± 124
Zn	220 ± 10	250 ± 48

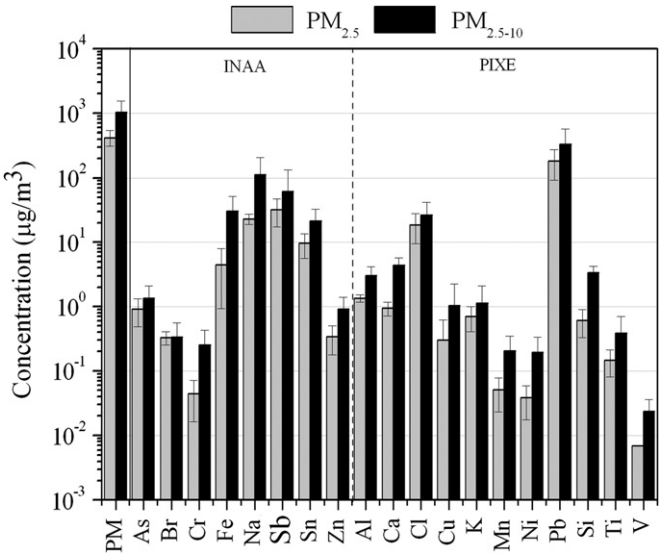

Fig. 1. Average element mass concentration in particulate matter sampled in a foundry workplace (values in μg/m^3).

The combination of k_0-INAA and PIXE allowed to assess the exposure of workers from the foundry industry, since together could give information for about 19 elements. Fig. 1 presents the particulate matter total and element mass concentration measured in the selected foundry workplace.

The high loadings of elements, which can be observed in Fig. 1, introduced some difficulties in the analyses of these filters by k_0-INAA. The huge amount of Sb in the filters elevated the spectra baseline, increasing the background, and consequently hindering the identification of weak photopeaks. The photopeak at 1115.5 and 1099.2 keV, which corresponds to the gamma rays of ^{65}Zn and ^{59}Fe, were hardly discernable due to the strong Compton background. Table 2 shows that, when these filters were analyzed, the detection limit for Zn and Fe increased significantly compared with the detection limit for environmental filters.

In order to solve this problem the Compton Suppression System was used in order to reduce the background of the gamma-ray spectra and, consequently, to lower the detection limits for radionuclides characteristic of the main single gamma-ray emission. The Compton suppression decreased the high background leading to a reduction of at least one order of magnitude, and consequently decreased the detection limits for Zn and Fe, which made possible their quantification in this study (Table 2).

4. Discussion

The average $PM_{2.5}$ and $PM_{2.5-10}$ total mass concentrations measured in the industry were 420 and 1000 μg/m^3, respectively. These concentrations did not exceed the limit value of 3000 μg/m^3 established, by the Portuguese Norm NP1796 [10] for PM_{10}.

Fig. 1 shows that the elements, which occurred with higher concentrations (> 10 μg/m^3) in the workplace were Pb, Sb, Fe, Sn, Na and Cl. Significantly higher element concentrations were measured inside the industry compared with outdoor environment levels (10,000 times higher for Pb and Sb, 1000 times higher for As and Na and 100 times higher for Br, Cl, Fe and Ni) [11]. It was also observed that coarse fraction ($PM_{2.5-10}$) was dominant for all the elements. This fact was expected as in the workplace sampling was made near the emission source and, consequently,

Table 2
Detection limits for Zn and Fe with and without Compton suppression (ng/m^3).

Type of filters System	Environment Without Compton suppression	Industry Without Compton suppression	Industry With Compton suppression
Zn	2.2	200	110
Fe	42	4900	1700

the deposition of the coarse and heavy particles have not yet occurred.

Element concentrations were compared with the limit values established by the Portuguese NP1796 for occupational exposure to chemical agents. It was verified that Pb levels exceeded the limit value of $50\,\mu g/m^3$ established by the norm for Pb in total suspended particles.

5. Conclusions

These results showed that the combination of k_0-INAA and PIXE was advantageously used to assess the exposure of workers from the foundry industry, because together could give information for about 19 elements. However, the determination of the particulate matter elemental composition in industrial environment was not a trivial task and faced difficulties due to the high contents of elements, which raised the spectra's backgrounds and increased the detection limits. The application of the Compton Suppression System was successfully performed since detection limits for Zn and Fe decreased.

Results showed that workers in this foundry plant were exposed to high concentrations of metals. In order to reduce the workers exposure, mitigation actions should be applied, in particular towards Pb, since it was verified that concentrations for this element exceeded the limit value established by the Portuguese NP1796 for occupational exposure to chemical agents.

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References

[1] M.C. Freitas, M.A. Reis, A.P. Marques, S.M. Almeida, M.M. Farinha, O. De Oliveira, M.G. Ventura, A.M.G. Pacheco, L.I.C. Barros, J. Radioanal. Nucl. Chem. 257 (2003) 621.
[2] S.M. Almeida, M.C. Freitas, M.A. Reis, C.A. Pio, J. Radioanal. Nucl. Chem. 257 (2003) 609.
[3] S.M. Almeida, M.C. Freitas, M.A. Reis, C.A. Pio, M.A. Trancoso, Nucl. Instr. and Meth. Phys. Res. A 564 (2006) 752.
[4] M.C. Freitas, S.M. Almeida, M.A. Reis, M.G. Ventura, J. Radioanal. Nucl. Chem. 262 (2004) 235.
[5] S.M. Almeida, M.C. Freitas, C.A. Pio, J. Radioanal. Nucl. Chem. 276 (2008) 161.
[6] W. Maenhaut, Co-ordinated Research Program: CRP E4.10.08, IAEA, Belgium, 1992.
[7] S.A.E. Johansson, J.L. Campbell, K.G. Malmqvist, Particle-Induced X-ray Emission Spectrometry (PIXE), John Wiley & Sons, 1995.
[8] R. Cornelis, J. Hoste, A. Speecke, C. Vandecasteele, J. Versieck, R. Gijbels, Activation Analysis, Part 2, 1976.
[9] F. De Corte, The k_0-Standardization Method—A Move to the Optimization of Neutron Activation Analysis, Agregé Thesis, Gent, 1987.
[10] Portuguese Norm NP 1796, Occupational Exposure Limits to Chemical Agents, Instituto Português de Qualidade, Portugal, 2007.
[11] S.M. Almeida, C.A. Pio, M.C. Freitas, M.A. Reis, M.A. Trancoso, Atmos. Environ. 39 (2005) 3127.