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Assessment of gold exposure and contamination in galvanizing workplace by neutron activation analysis

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Gold is not included in the current list of elements considered essential to humans and there are many controversies related to its toxicity. According to the chemical characteristics of the element, Au^{1+} is favored for binding at sites with S donor, such as sulfhydryl group (-SH) in proteins in biological systems. This tendency raises the possibility of health-related risk, mainly linked to a long-term exposure to high and low levels of gold. This paper highlights the determination of gold by instrumental neutron activation analysis (INAA) during the assessment of exposure levels to metals and possible workers' contamination in three galvanizing factories applying the same processes. This assessment is aimed at giving support to Worker's Health Awareness Program of the Municipal Department of Health of Belo Horizonte, Minas Gerais, Brazil. INAA, mix of k_0 and monostandard methods was applied to air filter, hair and toenail samples, and to urine samples. Solvent extraction of gold was carried out followed by comparative INAA. The results revealed that gold was present in all matrixes, indicating the exposure in the workplace and suggesting endogenous contamination. Is gold playing a role as a toxic element?

Introduction

The workplace is an example of a long-term exposure not only to high but also to low levels of several elements. The presence of toxic substances in the workplace requires a systematic evaluation of the degree of exposure and health status of exposed subjects. Nevertheless, in spite of this the worker's health service is guided to look for risks in the workplace and the measurement of the level of elements in human organism is usually done by analyzing human fluids, such as blood and urine. These biological materials are often considered the best way to evaluate undue exposure, but the results reflect a transient situation.[1–5]

This work is related to a health assessment in a galvanizing industry and its goal was to make a survey of the exposure to metals according to two approaches: (1) the characterization of the work environment assessing airborne particulate matter and (2) biomonitoring hair, toenail and urine from exposed workers.[5–11]

This assessment also had as its objective to alert the Worker's Health Awareness Program of the Secretaria Municipal de Saúde (Municipal Department of Health) of Belo Horizonte, Minas Gerais, for the need of a study about long-term exposure to pollutants in the workplace associated with the worker's contamination. Up to now, this has not been the health program task. Galvanizing industry was chosen as the object of this study concerning health risks since the majority of patients who look for medical assistance because of metal contamination are hired by the galvanizing industry. It is important to mention that this project was approved by the Ethics Committee of the Federal University of Minas Gerais, COEP-UFMG. Several elements were determined in this assessment[6–10] but this paper will emphasise and describe only the determination of gold.

This study focuses on gold as this element is not included in the current list of elements considered essential to humans.[12,13] Concerning toxicity, the literature has reported few cases of injury to skin and mucous membranes caused by this metal. There are some cases related to acute dose cases during chrysotherapy.[14,15] The metabolites generated from gold drugs have not been identified positively and the knowledge on the mechanisms of action is still inaccurate. Gold toxicity to human beings has not been proved because of many controversies.[16]

On the other hand, according to the hard-soft principle, gold is defined as a soft acid meaning that it prefers to co-ordinate with soft bases.[17] In biological systems, Au^{1+} is favored for binding at sites with S donor, such as sulfhydryl group (-SH) in proteins. This tendency raises the possibility of health-related risk, mainly linked to a long-term exposure to high and low levels of gold.

Experimental

Place study

Galvanization[8,11] is an electroplating process of depositing a coating on a desirable form by means of electrolysis. To develop this project, galvanization factories working with the same procedures, as the

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"decorative chromium", were selected. "Decorative chromium" means that various kinds of electrodeposition are applied involving chromium, gold, silver, copper and other metals. The plating is usually cover small items like taps, trays and decorative items. In Belo Horizonte this kind of factory is called home factory because they are located in a small warehouse, operated by 3 to 10 workers and the industrial process does not demand a complex structure to be installed, involving low maintenance costs and inexpensive available labor force.

Galvanizing factory hires item cleaners, who wash the materials with water, dry them with sawdust and also execute other tasks such as organizing the clients' orders and cleaning the areas. Platers are responsible for the chemical cleaning of items and the electrodeposition. Polishers handle all the items before the electrodeposition, polishing them either manually or mechanically. The items prepared to be plated have usually been previously covered with other metals.

According to strategic planning three galvanizings, G1, G2 and G3, were studied and chosen at random in downtown Belo Horizonte.

Airborne particulate matter sampling and preparation

In order to evaluate the level of elemental concentration in the indoor environment of the plants, stationary air sampling was carried out.[8–10] The sampling of airborne particulate matter (APM) was conducted by using filters of 0.8-μm pore size to get the breathable fraction, and 5.0-μm pore size to get the inhalable fraction. Both filters were housed in polystyrene cassettes. Each of the two samplers, one with 0.8-mm pore size and another with 5.0-μm pore size, would collect the APM simultaneously at the same place during a one-day working hours at 4 $l \cdot min^{-1}$. As the primary objective of the study was to obtain information regarding workers' exposure, the samples were collected from places that would reflect, as much as possible, the indoor environment. After the sampling, the cassettes were carefully opened. The air filters were folded and inserted into their respective polyethylene tube for irradiation. The samples were collected only once according to the strategy chosen.[7,8]

Biomonitors sampling and preparation

As already reported in other papers,[7–10] the sampling of the Workers' Group was carried out after the physicians had explained to the workers the aims of the project and how it would be performed. The volunteer workers (26 males) donated hair samples, toenail clippings and also urine.

The scalp hair samples were collected by a professional hairdresser and the procedure was according to IAEA instructions,[18] from the nape with scissors. All hair samples were washed following the IAEA procedure.[18] After washing, the samples were dried at 40 °C and weighed in the irradiation container.

The toenails samples were washed using the procedure in the literature.[19] After washing, the samples were air dried and weighed in the irradiation container.

The urine donated by the workers was collected on the last work day of the week and at the end of the shift. Urine was also collected the next Monday, just before work began because of the metal elimination rate.[5] Instructions were followed in order to avoid external contamination. This biomonitor was also donated by the comparative group, made up of 22 subjects not exposed to the same workplace environment. The urine samples were collected in polyethylene flasks and an aliquot of 5 ml was taken to determine the creatinine concentration. The samples were lyophilized in order to concentrate the minerals present. It is important to mention that no other aspect such as diet and personal habit was controlled.

Application of instrumental neutron activation analysis

Airborne particulate matter in air filters, hair and toenail samples: k_0-monostandard method: The irradiation was performed in the reactor Triga Mark I IPR-R1 in the Nuclear Technology Development Centre/Nuclear Energy National Commission (CDTN/CNEN), at 100 kW, under a thermal neutron flux of $6.6 \cdot 10^{11}$ $n \cdot cm^{-2} \cdot s^{-1}$. The samples were irradiated simultaneously with Au and Na standards as comparators, and Human Hair reference certified material,[20] GBW 09101, from the Shanghai Institute of Nuclear Research. The usual neutron activation analysis and gamma-spectroscopy comprises schemes of irradiation time, producing radionuclides under reaction (n,γ): 5 minutes and 10 hours of irradiation time and suitable decay and measurement time to determine several elements. Gold was determined after 4-hour irradiation, based on its radionuclide ^{198}Au ($T_{1/2} = 2.7$ d). The gamma-spectroscopy was performed in a HPGe detector with 15% efficiency and resolution of 1.85 keV for the 1332 keV peak of ^{60}Co. The concentration was calculated based on k_0 constants and equations.[21–24]

Urine samples: comparative method: The same procedure to determine gold in lyophilized urine samples would be applied. But due to matrix interference, from the high activity induced in the sample mainly from Na and K, urine component, it was decided to separate gold from these interferences by

chemical procedures. A solvent extraction of gold using methyl isobutyl ketone (MIBK)[25] was applied to the samples, to several gold standards prepared from gold foil (specpure, Johnson Matthey Chemicals Ltd., UK) and to the certified reference material SRM 2670, Freeze-Dried Urine.[26]

The first step was to transfer each sample, gold standard and reference material to a beaker with 25 ml of deionized water and to proceed with the organic digestion using 3 ml of H_2O_2, under 100 °C, until the solution was totally clear. The volume was reduced to 3 ml and then 15 ml of a solution of $HCl:HNO_3$, 3:1 and 1 ml of H_2O_2 were added. Under heating, the solution was again reduced to 3 ml and 20 ml of 50% HCl, was added. Again the volume was reduced to 3 ml and the solution was transferred to a 25 ml separating funnel. The solvent MIBK (25 ml) was added and the flask was shaken for 10 minutes. A volume of 7 ml from organic layer was collected into an irradiation tube. This organic phase was completely evaporated under slow heating. In other tubes gold standards were pipetted and also evaporated without any chemical procedure.

The samples and gold standards were irradiated for 4 hours, reaching the activity of 74 Bq corresponding to the lowest gold concentration standard. After suitable decay time, gamma-spectra were acquired under the same geometry. After decay correction, the gold elemental concentration was calculated by linear regression. The chemical yield related to the extraction step was 99%.

Results and discussion

Table 1 presents the concentration of gold determined in airborne particulate matter. For this element there is not a threshold limit value (TLV) foreseen, that "refers to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed to day after day without any adverse health effects" according to the definition of the American Conference of Governmental Industrial Hygienists, ACGIH.[27]

The results show that gold was present in the polishing and bath areas in Galvanizing 1 (G1), pointing out that it has originate from the previous coating on the items, spread everywhere during the polishing procedure, because gold is not electrodeposited in this factory.

On the other hand, Galvanizing 2 (G2) electroplates Au, among other elements. The bath area, support preparation, acid cleaning and reception desk are located on the ground floor without any physical separation. Consequently, the amount of gold determined came from the electodeposition process reaching the reception desk. The polishing area is on the second floor and the results revealed that gold in airborne particulate matter collected came only from the previous coating on the items during the polishing process. There is no physical communication between the polishing and the other areas.

In Galvanizing 3 (G3), the galvanizing process causes the worse distribution of gold because there is physical communication between the processes.[8,10] The high concentration values are shown in Table 1 and confirm the indoor pollution. It is not possible to evaluate exactly the contribution of the polishing and bath areas from these high values.

Table 2 presents the concentration results for biomonitors and for reference materials. The highest values determined in the workers' samples were much higher than those determined for non exposed subjects. It is possible to observe that the highest concentration values were found in biological samples from workers hired by G3, exactly the factory that offered the highest related risk-health.[6,8,10] The urine sample donated by the worker in charge of gold plating at G2 presented the highest value confirming the excessive exposure to gold during electrodeposition.

Table 1. Concentration of gold (in $\mu g \cdot m^{-3}$) in airborne particulate matter

Factory	TLV	Reception desk		Office		Bath area		Polishing area	
		Breathable fraction	Inhalable fraction	Breathable fraction	Inhalable fraction	Breathable fraction	Inhalable fraction	Breathable fraction	Inhalable fraction
G1	NF	ND	ND	No office		0.002± 0.002	0.0001 ± 0.0004	0.04 ± 0.01	0.07 ± 0.01
G2	NF	0.09 ± 0.02	0.022± 0.001	No office		0.04 ± 0.01	0.030 ± 0.002	0.07 ± 0.01	ND
G3	NF	366 ± 1	4.0 ± 0.1	2 ± 1	2.0 ± 0.2	3.0 ± 0.2	10.0 ± 0.2	67 ± 1	12 ± 1

TLV: Threshold limit value.
NF: Not foreseen.
ND: Not detected.

Table 2. Concentration of gold in biomonitors – comparative and worker's groups

Matrix	DL	Reference material		Comparative group (22 individuals)	Galvanizing 1 (9 workers)	Galvanizing 2 (9 workers)	Galvanizing 3 (7 workers)
		This work	Certified	Range mean; *n*	Range median; *n*	Range average; *n*	Range average; *n*
Hair, $\mu g \cdot g^{-1}$	0.007	Human hair GBW 0901[20]		0.002 – 0.3	0.024 – 0.2	0.05 – 0.8	0.03 – 4.48
		ND	NR	0.002 ×÷ 4; 12	0.1 ×÷ 1.3; 8	0.4 ×÷ 1.4; 9	0.5 ×÷ 2.0; 6
Toenail, $\mu g \cdot g^{-1}$	0.001	No reference material		0.01 – 0.04	0.008 – 0.2	0.002 – 0.09	0.092 – 0.68
				0.02 ×÷ 3.4; 6	0.02 ×÷ 1.8; 6	0.01 ×÷ 2; 9	0.2 ×÷ 1.4; 7
Urine, $\mu g \cdot g^{-1}$	0.001	Urine SRM 2670[26] ($\mu g \cdot ml^{-1}$)		<0.001	<0.001 – 5	<0.001 – 17	<0.001 – 13
creatinine		220 ± 20	240 i		1.3 ×÷ 0.5; 4	17 ± 2; 1	9 ± 4; 2

DL: Detection limit.
ND: Not detected.
NR: Not reported.
i: Informative value.
n: Number of individuals whose samples presented gold.

Conclusions

The analytical technique applied, the instrumental neutron activation analysis (k_0-monostandard and comparative methods) confirmed its status as one of the most versatile techniques. Its application to air filter, hair and toenail without solubilization of the sample, is very important avoiding possible contamination and loss of sample. Solubilization is a sine qua non condition of other techniques as atomic absorption spectrophotometry or inductively-coupled plasma-mass spectrometry (ICP-MS). The application of the comparative neutron activation method to urine samples, following a classical method of solvent extraction, reinforces its characteristics as a versatile technique.

The results obtained in airborne particulate matter collected in air filters pointed out that the polishing area as workplace is offering the highest pollutant exposure risks to workers. It does not matter if gold is plated or not in the factories. In factories where gold plating is processed, there is an additional risk of exposure and, consequently, endogenous contamination.

The general assessment of risks reveals the level of exposure to gold and exposes the danger of hidden gold as there is neither TLV nor any knowledge of its risks to man's health. This investigation project was the first action in order to assess the elemental concentration of gold in a galvanizing industry. So far gold had not been pointed out in this kind of workplace neither in airborne particulate matter nor in biomonitor. The results revealed that gold was present in all matrices, pointing out the exposure in the workplace and suggesting endogenous contamination. The concentrations in the workers samples are higher than the content in the samples of comparative group. Since the urine is a biomonitor often considered the best way of evaluating undue exposure, the high gold concentrations determined in urine samples reinforce the suggestion of endogenous contamination.

Since gold is not considered essential for human beings, is it playing a role as a toxic element?

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