ELEMENTAL CONCENTRATIONS IN AIR AND DRINKING WATER INSIDE A FERTILIZER PLANT IN ROMANIA DETERMINED BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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Abstract

The elemental concentrations of Ag, Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, F, Fe, Hf, Hg, I, K, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, Zn, and Zr in airborne particulate matter (PM10), deposited dust, and tap water samples collected inside a phosphate fertilizer plant in Romania have been determined by Instrumental Neutron Activation Analysis (INAA). In addition, X-Ray Fluorescence Analysis (XRFA) was used to determine S, and also Ba, Mn, and Ti in airborne particulate mater. These results were compared with permissible levels given by the Romanian norms for chemical pollutants in the workplace atmosphere and potable water. All values were below the maximum permissible levels.

Introduction

The processing of phosphate rock and pyrite into phosphoric and sulphuric acid has significant impacts to the environment of the processing industry and also result to exposure of the employees to relatively high levels of uranium and the lanthanoides [1]. These potentially toxic elements can reach and contaminate human organisms via air particulate matter and drinking water. A study was therefore carried out to assess the impact of fertilizer plants in Russia, Poland, Romania, and Uzbekistan in the frame of a Copernicus project [2]. The research in Romania was focused on the TURNU phosphate fertilizer plant, situated in the vicinity of the town Turnu Magurele, on the Danube shore.

Instrumental Neutron Activation Analysis (INAA) was used to determine concentrations of major, minor and trace elements in the workplace atmosphere (PM10 and deposited dust) and in drinking water samples collected from this plant. The results can be compared with the maximum permissible levels given by the Romanian norms for chemical pollutants in the workplace atmosphere [3] and potable water [4].

Experimental

Airborne particulate mater (<10 μm) was continuously collected on aerosol filter during one week, at the H_3PO_4+NPK1 shop of the fertilizer plant, at a sampling rate of about 1.5 $m^3 \cdot h^{-1}$ [5]. The air volume passing the filter was 245 m^3 and mass of dust collected was about 370 mg, corresponding to a dust concentration in air (PM10) of 1.5 $mg \cdot m^{-3}$.

Deposited dust and tap water samples were collected from five shops of the plant (H_3PO_4 + NPK1, H_2SO_4, Urea 1, Urea 2, and NPK2).

1 L of water was first concentrated at 65 ˚C and 0.20 bar using a rotating evaporator (VV2000 Heidolph Co.) to a volume of about 30 cm^3, then dried on polyethylene foils under light bulb in a ventilated space [6]. The amount of dry residues varied from about 240 to 330 $g \cdot L^{-1}$.

INAA based on the measurement of radionuclides with long half-lives was applied at IFIN-HH in Magurele for all investigated samples using the TRIGA reactor in Pitesti. INAA using radionuclides with short half-lives was done with the IBR-2 reactor at JINR in Dubna for the deposited dust samples and with the HOR reactor at TU Delft for the aerosol filter and tap water (H_2SO_4 shop) [6].

XRFA was applied at the Institute of Physics and Meteorology of the University of Hohenheim in Stuttgart (Germany) to analyze the aerosol filter, by Finnigan XRF analyzer with Rh tube excitation and Si(Li) detector [5].

Results and discussion

The elements Ag, As, Au, Ba, Br, Ca, Cd, Co, Cr, Cs, Fe, Hf, Hg, K, Mo, Na, Nd, Ni, Rb, Sb, Sc, Se, Sr, Ta, Th, U, W, Zn, Zr, and lanthanoides (Ce, Eu, La, Lu, Nd, Sm, Tb, Yb, and Sc) in the examined samples could be determined by INAA via the radionculides with long half-lives and the elements Al, Cl, Cu, Dy, F, I, Mg, and V in aerosol filter, as well as Al, Cl, Cu, I, Mg, Mn, Ti, and V in dust deposition, and Cl, I, Mg, Mn, S, Si, and V in water samples were determined by INAA via measurement of the radionuclide with short half lives.

Corrections were done for the uranium fission interference in analyzing Ba, Ce, La, Mo, Nd, and Zr, as well as for spectral interference of Sm with Pu $K_{\alpha 1}$ X-ray (^{239}Pu is formed by β^- decay of ^{239}Np, produced by $^{238}U(n,\gamma)\beta^-$ reaction) [7].

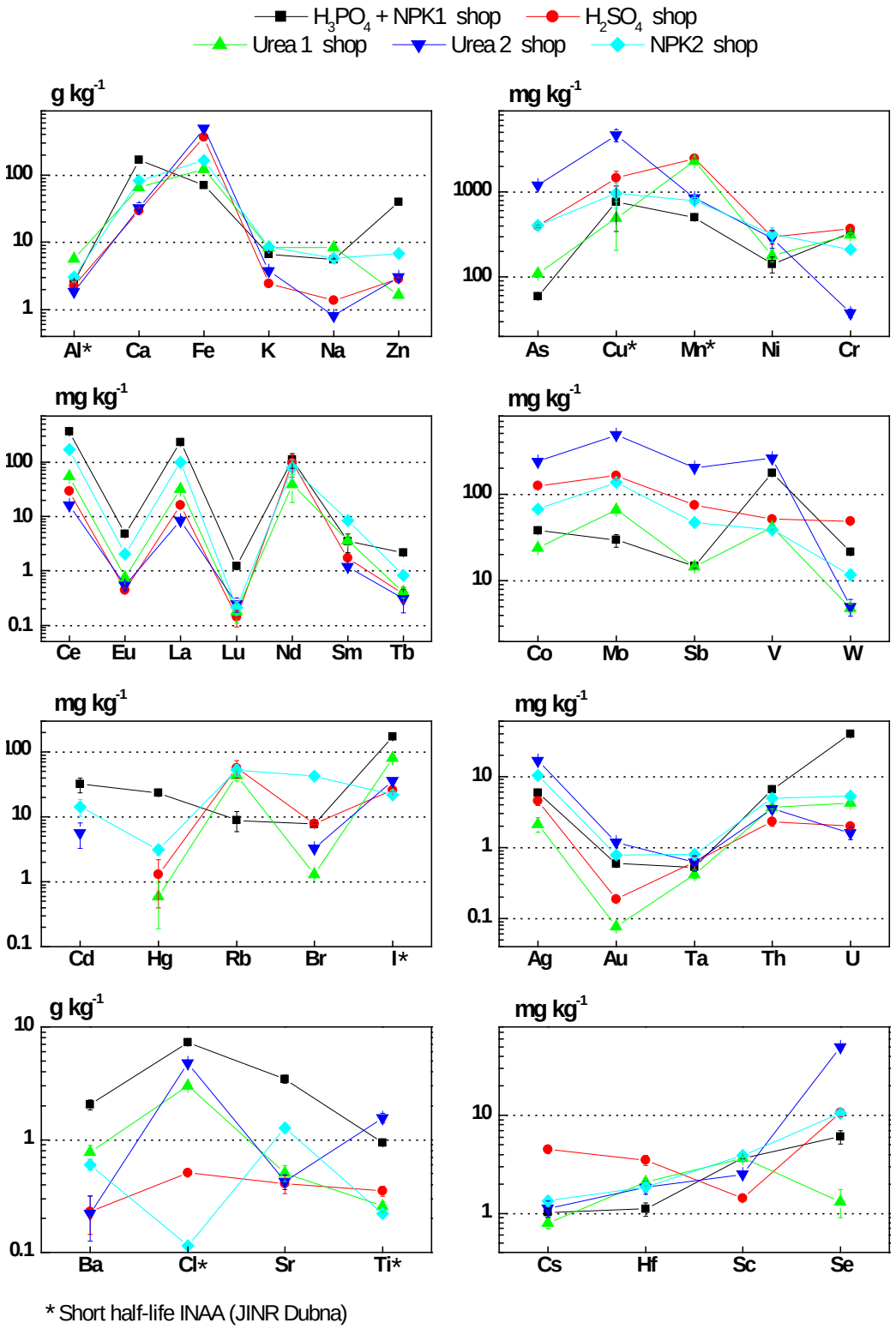
The elemental concentrations in airborne particulate matter are given in Table 1 together with values of the maximum permissible levels in Romania for the workplace atmosphere [3]; the results from the analysis of the tap water collected from the H_2SO_4 shop are given in Table 2 together with values of the maximum permissible levels in Romania for potable water [4]. The combined standard uncertainties (± 1σ) in both tables are based on the contributions from the counting uncertainties of sample and standard, and the uncertainty in the concentration of the standard. Detection limits are based on a virtual peak with an area equivalent to 3σ of the background. Fig. 1 comparatively shows elemental concentrations determined for 41 elements in the deposited dust; in addition, Mg and Yb could be determined in the dust samples (concentrations between 8.4 and 15 $g \cdot kg^{-1}$, and between 0.6 and 5.6 $mg \cdot kg^{-1}$, respectively).

The elemental concentrations measured in inhalable dust (< 10 μm) from the H_3PO_4+NPK1 shop of the fertilizer plant (Table 1) do not exceed the permitted levels given by the Romanian norms for Ag, Al, As, Ba, Br, Ca, Cd, Cl, Cr, Cu, F, Fe, Hf, Hg, I, Mg, Mn, Mo, Ni, Sb, S, Se, Th, Ti, V, W, and Zn in the workplace atmosphere [3]. Mass of suspended matter in air (1.5 $mg \cdot m^{-3}$) was found about ten times lower than the maximum permissible levels [3].

Table 1. Elemental concentrations in airborne particulate matter collected inside the fertilizer plant (H_3PO_4+NPK1 shop) determined by INAA and XRFA, and permissible levels in Romania ($ng \cdot m^{-3}$; * $\mu g \cdot m^{-3}$).

Elem.	Airborne particulate matter	Permissible level [3]	Elem.	Airborne particulate matter	Permissible level [3]
Ag	5.8 ± 0.6	$1.5 \cdot 10^4$	Lu	1.14 ± 0.08	
Al	3800 ± 600		Mg	5400 ± 400	$1.5 \cdot 10^7$ (MgO)
As	340 ± 10	$5 \cdot 10^5$	Mn	39 ± 2 [(a)]	$3 \cdot 10^6$
Au	0.15 ± 0.02		Mo	113 ± 14	$5 \cdot 10^6$
Ba	201 ± 10 [(a)]	$5 \cdot 10^5$	Na	3560 ± 70	
Br	9.5 ± 0.7	$1 \cdot 10^6$	Nd	33 ± 14	
* Ca	220 ± 10	$5 \cdot 10^3$ (CaO)	Ni	90 ± 30	$1.5 \cdot 10^6$
Cd	18 ± 6	$2 \cdot 10^5$ (oxides)	Rb	5 ± 2	
Ce	32.6 ± 1.0		Sb	39.7 ± 1.0	$5 \cdot 10^5$
* Cl	14.6 ± 0.6	$2 \cdot 10^3$	S	102 ± 5 [(a)]	$1.5 \cdot 10^4$ (SO_2)
Co	17.8 ± 0.3		Sc	3.46 ± 0.09	
Cr	417 ± 15	$1 \cdot 10^5$ (CrO_3)	Se	10.1 ± 0.8	$2 \cdot 10^5$ [(b)]
Cs	0.46 ± 0.07		Sm	2.7 ± 0.4	
Cu	1170 ± 60	$1.5 \cdot 10^6$	Sr	1190 ± 70	
Dy	2.84 ± 0.13		Ta	< 0.1	$1 \cdot 10^7$
Eu	1.11 ± 0.07		Tb	0.52 ± 0.07	
* F	45.7 ± 1.1	$2 \cdot 10^2$	Th	2.4 ± 0.1	$5 \cdot 10^4$
* Fe	44.3 ± 0.6	$1.5 \cdot 10^4$ (Fe_2O_3)	Ti	560 ± 20 [(a)]	
Hf	0.53 ± 0.07	$5 \cdot 10^5$	U	58 ± 4	
Hg	0.6 ± 0.6	$1.5 \cdot 10^5$	V	162 ± 4	$5 \cdot 10^5$ (V_2O_5)
I	690 ± 20	$1 \cdot 10^6$	W	1.7 ± 0.5	$6 \cdot 10^6$
K	1900 ± 300		Yb	3.3 ± 0.3	
La	32.8 ± 0.6		Zn	860 ± 20	$1 \cdot 10^7$ (ZnO)

[(a)] XRFA values for Ba, Mn, S, and Ti; [(b)] Se compounds.



* Short half-life INAA (JINR Dubna)

Fig. 1. Elemental concentrations in deposited dust collected from five shops of the fertilizer plant.

Table 2. Elemental concentrations in tap water collected from the H_2SO_4 shop of the fertilizer plant and permissible levels in Romania.

Element	Conc. value	Permissible level [4]	Element	Conc. value	Permissible level [4]
Ag ($ng \cdot L^{-1}$)	28 ± 14		Mo ($ng \cdot L^{-1}$)	160 ± 30	
As ($\mu g \cdot L^{-1}$)	1.2 ± 0.3	50	Na ($mg \cdot L^{-1}$)	41.7 ± 0.8	
Au ($ng \cdot L^{-1}$)	< 6		Nd ($ng \cdot L^{-1}$)	340 ± 150	
Ba ($\mu g \cdot L^{-1}$)	39 ± 4		Ni ($\mu g \cdot L^{-1}$)	2.2 ± 0.4	100
Br ($\mu g \cdot L^{-1}$)	53 ± 2		Rb ($\mu g \cdot L^{-1}$)	2.2 ± 0.3	
Ca ($mg \cdot L^{-1}$)	50 ± 2	100	S ($mg \cdot L^{-1}$)	< 300	
Ce ($ng \cdot L^{-1}$)	270 ± 40		Sb ($ng \cdot L^{-1}$)	410 ± 20	
Cl ($mg \cdot L^{-1}$)	68.8 ± 1.3		Sc ($ng \cdot L^{-1}$)	1.5 ± 0.2	
Co ($ng \cdot L^{-1}$)	60 ± 4		Se ($ng \cdot L^{-1}$)	110 ± 20	10000
Cr ($\mu g \cdot L^{-1}$)	0.21 ± 0.02	50	Si ($mg \cdot L^{-1}$)	< 300	
Eu ($ng \cdot L^{-1}$)	2.6 ± 0.8		Sm ($ng \cdot L^{-1}$)	120 ± 20	
Fe ($\mu g \cdot L^{-1}$)	5.7 ± 1.0	100	Sr ($\mu g \cdot L^{-1}$)	240 ± 30	
Hg ($ng \cdot L^{-1}$)	9 ± 6	1000	Ta ($ng \cdot L^{-1}$)	26 ± 10	
I ($\mu g \cdot L^{-1}$)	< 13		Th ($ng \cdot L^{-1}$)	< 5	10000 [(a)]
K ($mg \cdot L^{-1}$)	4.5 ± 0.8	400 [(a)]	U ($\mu g \cdot L^{-1}$)	1.4 ± 0.2	21
La ($\mu g \cdot L^{-1}$)	< 0.7		V ($\mu g \cdot L^{-1}$)	< 60	
Mg ($mg \cdot L^{-1}$)	13.0 ± 0.7	50	Zn ($\mu g \cdot L^{-1}$)	21.4 ± 0.7	5000
Mn ($\mu g \cdot L^{-1}$)	< 2	50	Zr ($\mu g \cdot L^{-1}$)	9.1 ± 1.0	

[(a)] K and Th concentrations were calculated from ^{40}K and ^{232}Th radioactivity levels of 13.4 $Bq \cdot L^{-1}$ and 0.04 $Bq \cdot L^{-1}$, respectively.

The elemental concentrations determined by us in tap water samples collected from this factory (Table 2) are lower than the permissible levels reported for As, Ca, Cr, Fe, Hg, K, Mg, Mn, Ni, Se, Th, U, and Zn in potable water [4].

Conclusions

INAA proved to be a powerful analytical technique able to determine 45 elements (Ag, Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, F, Fe, Hf, Hg, I, K, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, and Zn) in airborne particulate matter, 43 elements in deposited dust and 36 elements in tap water samples.

Elemental concentration values determined in airborne particulate matter (PM10) and tap water from the TURNU phosphate fertilizer plant in Romania are situated below the maximum permissible levels in workplace atmosphere [3] and potable water [4].

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