

ELEMENTAL EVALUATION IN PLASTIC GARBAGE BAGS PURCHASED FROM LOCAL MARKETS IN PIRACICABA, SÃO PAULO STATE, USING THE EDXRF TECHNIQUE

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ABSTRACT

Plastic garbage bags have been used for packing household waste in Piracicaba city and nearby cities broadly. Many of these bags are made from recycled polymers and the presence of harmful elements is a matter of concern. In this work fourteen plastic garbage bags of different brands and colors were purchased from local markets in Piracicaba, State of São Paulo. For the analysis, the samples in triplicate were cut into 47 mm diameter circle and attached into acrylic holder and analyzed directly by Energy Dispersive X-Ray Fluorescence - EDXRF. The excitation was carried out using an X-ray tube Mo target and Zr filter (15 kV / 25 mA) under non-vacuum. The characteristic X-rays were detected by a semiconductor detector Si(Li), coupled to a multichannel analyzer system. The acquisition time was 500 s and the X-ray spectra were deconvoluted by the AXIL software. For quantification it was used a standard set produced by the MicroMatter/USA and the absorption effect was corrected by the known chemical composition matrix technique, in which allowed the determination of K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Sr by $K\alpha$ lines and Pb by the line $L\alpha$ simultaneously. The trueness of the method was verified by analyzing a certified reference material (NIST air particulate on filter media, SRM2783). The limits of detection (LD) for these elements were: K - 38.9; Ca - 19.4; Ti - 7.1; Cr - 3.1; Mn - 2.1; Fe - 1.5; Cu - 0.86; Zn - 0.85; Sr - 4.6 and Pb - 2.8 $\mu\text{g g}^{-1}$. Some elements showed minimum and/or maximum concentrations well above the LDs, as K: <LD - 240; Ca: 130 - 8900; Ti: 1002 - 8600; Cr: <LD - 63; Mn: <LD - 23; Fe: 40 - 390; Cu: 2.0 - 245; Zn: 19 - 167; Sr: <LD - 11 and Pb: <LD - 130 $\mu\text{g g}^{-1}$.

Keywords: EDXRF, XRF, chemical composition, plastic garbage bag, simultaneous analysis, non-destructive analysis, multielemental analysis.

1. INTRODUCTION

Piracicaba city produces 213 tons of household waste on a daily basis, in which all of it is disposal in a not public landfill in a nearby city, Paulínia/SP, roughly 62 km away [1]. It is a common practice the use of plastic garbage bags for packing household waste in Piracicaba city and also in nearby cities. Many of these bags are made from recycled polymers and the presence of harmful elements is a matter of concern. It should be mentioned that the landfill for household waste is not supposed to be a harmful waste disposal. The aim of this work was to use the EDXRF technique for a direct, non-destructive, multielemental and simultaneous analysis to verify the presence of possible harmful chemical elements in plastic garbage bags from Piracicaba local market.

2. EXPERIMENTAL

2.1. Sample preparation and experimental set up

Fourteen plastic garbage bags of different brands and colors were purchased from local markets in Piracicaba, State of São Paulo. Samples were cut into 47 mm diameter circle in triplicate and attached into acrylic holder. The calibration standards and samples were analyzed directly by Energy Dispersive X-Ray Fluorescence (EDXRF).

2.2. EDXRF analysis

The excitation was carried out using an X-ray tube Mo target and Zr filter (15 kV / 25 mA) under non-vacuum. The characteristic X-rays were detected by a semiconductor detector Si(Li), coupled to a multichannel analyzer system. The acquisition time was 500 s for calibration standards and samples. The X-ray spectra were deconvoluted by the AXIL software [2].

2.3. Elemental Quantitative Analyses

For EDXRF sample analysis using monoenergetic X-ray excitation, the characteristic $K\alpha$ X-ray intensity I_i (cps) is given by [3-4]:

$$I_i = S_i \cdot C_i \cdot A_i \quad (1)$$

where S_i = elemental sensitivity (cps $\mu\text{g}^{-1} \text{cm}^2$), C_i = elemental superficial concentration ($\mu\text{g cm}^{-2}$) and A_i = absorption factor (unitless) of the sample for the analyte, given by:

$$A = \frac{1 - e^{-\chi \cdot \rho_o \cdot D}}{\chi \cdot \rho_o \cdot D} \quad (2)$$

where ρ_o and D = polyethylene density (g cm^{-3}) and sample thickness (cm), respectively, and χ = total mass absorption coefficient ($\text{cm}^2 \text{g}^{-1}$), given by equation [3-4]:

$$\chi = \mu_0 / \text{sen}\theta_0 + \mu / \text{sen}\theta \quad (3)$$

where μ_0 and μ = mass absorption coefficient ($\text{cm}^2 \text{g}^{-1}$) of the sample for the excitation energy from the X-ray tube target and the characteristic X-ray energy of the analyte, respectively, and θ_0 and θ = excitation and detection angles, in which the incident and emergent beams are related to sample surface, respectively.

For elemental sensitivity S_i ($\text{cps } \mu\text{g}^{-1} \text{cm}^2$) determination it was analyzed thin film standard of known superficial concentration C_i ($\mu\text{g cm}^{-2}$), in which the characteristic $K\alpha$ X-ray or $L\alpha$ intensities I_i (cps) for higher atomic number Z elements, like Pb, was measured. For being a thin film, the thickness is considered close to zero and the absorption factor is considered unitary.

Then, superficial concentration C_i ($\mu\text{g cm}^{-2}$) was calculated through equation 1 by measuring the characteristic X-ray intensity I_i (cps) of the analyte in the sample, and sensitivity S_i ($\text{cps } \mu\text{g}^{-1} \text{cm}^2$) and absorption factor A_i (unitless) previous determined. Finally, the superficial concentration C_i ($\mu\text{g cm}^{-2}$) could be converted to normal concentration c_i ($\mu\text{g g}^{-1}$) in the sample by the equation:

$$c_i = \frac{C_i}{\rho_o \cdot D} \quad (4)$$

where ρ_o = density of the sample (g cm^{-3}). Experimentally instead of measure and use the terms ρ_o and D separately in the equations it is more practice to measure a sample area and respective weight, and calculate the superficial density $\rho_o \cdot D$ (g cm^{-2}) as mass/area.

2.4. Elemental sensitivity determination

To determine the sensitivity ($\text{cps } \mu\text{g}^{-1} \text{cm}^{-2}$) for the elements from K to Sr (by $K\alpha$ lines) and Pb (by the line $L\alpha$), it was used a XRF calibration standard set produced by MicroMatter / USA, containing one or two elements per standard (K = 26.7, Ca = 30.9, Sc = 21.9, Ti = 43.3, Mn = 60.0, Fe = 49.5, Cu = 42.3, Zn = 16.2, Se = 49.5, Sr = 32.7 and Pb = 48.3 $\mu\text{g.cm}^{-2}$).

2.5. Limit of detection

The limit of detection LD_i ($\mu\text{g g}^{-1}$) was calculated using Equation 5 [3-5]:

$$LD_i = \frac{3}{S_i \cdot \rho_o \cdot D} \sqrt{\frac{I_{i(BG)}}{t}} \quad (5)$$

where $I_{i(BG)}$ = background intensity under the peak analyte i (cps) and t = acquisition time (s).

3. RESULTS

Figure 1 shows the elemental sensitivity S_i dependence of atomic number Z . Through this correlation, the sensitivity was determined for the elements from K to Sr. It should be noted that S_i rises sharply for atomic number lower than 24. This is theoretically predicted in X-ray fluorescence for low atomic number elements due to both lower fluorescence yield, and air and Be window detector absorptions. Other feature is that the higher the X-ray energy, the lower is probability of interaction with the Si(Li) crystal in the detector, and so, this factor cause the worsening of the detection limit for Z higher than 33.

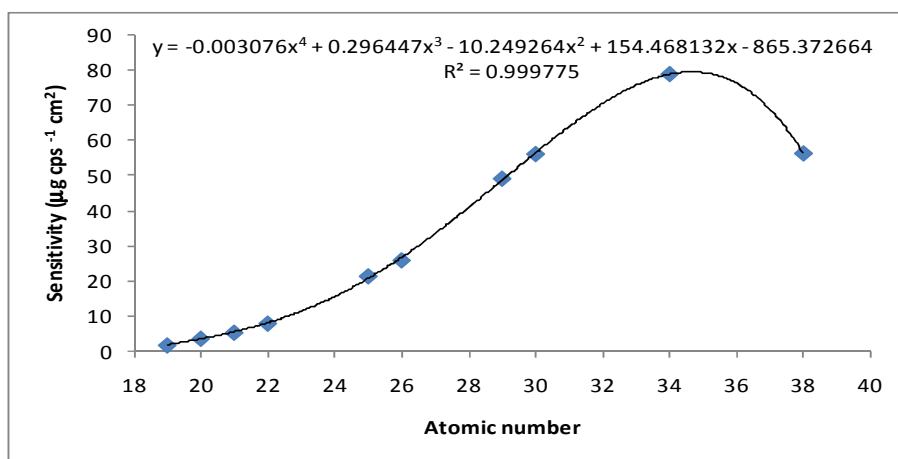


Figure 1. Elemental sensitivity S_i ($\mu\text{g cps}^{-1} \text{cm}^2$) dependence of atomic number Z .

Figure 2 shows the LD_i ($\mu\text{g g}^{-1}$) for elements from K ($Z = 19$) to Sr ($Z = 38$), taking into account the acquisition time of 500 s. The limits of detection for these elements were: K – 38.9; Ca – 19.4; Ti – 7.1; Cr – 3.1; Mn – 2.1; Fe – 1.5; Cu – 0.86; Zn – 0.85; Sr – 4.6 and Pb – 2.8 $\mu\text{g g}^{-1}$.

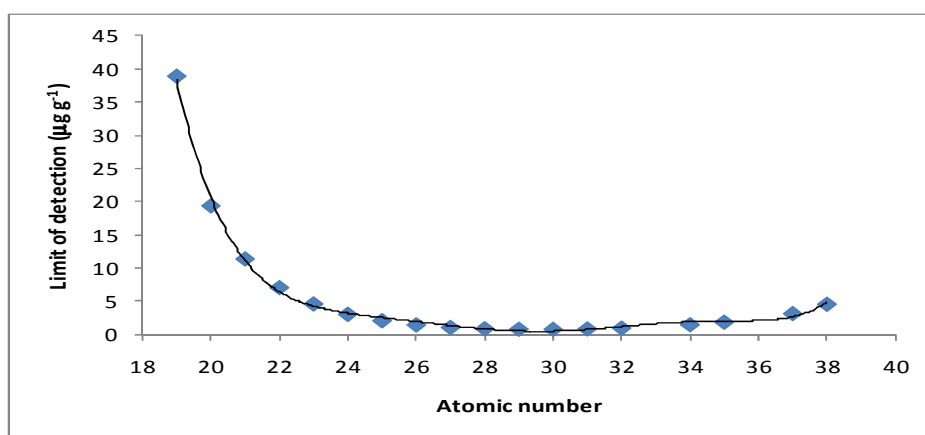


Figure 2. Limits of detection (LD_i , $\mu\text{g g}^{-1}$) for the elements K ($Z=19$) to Sr ($Z=38$) using a 500 s excitation time.

Figure 3 shows the X-ray spectra of the plastic garbage bag sample no. 9, containing mainly the elements Ca, Ti, Fe, Cu, Zn and Pb. The argon characteristic X-ray peaks are due to this element presence in the atmosphere (the EDXRF analyses were not carried out under vacuum nor controlled conditions).

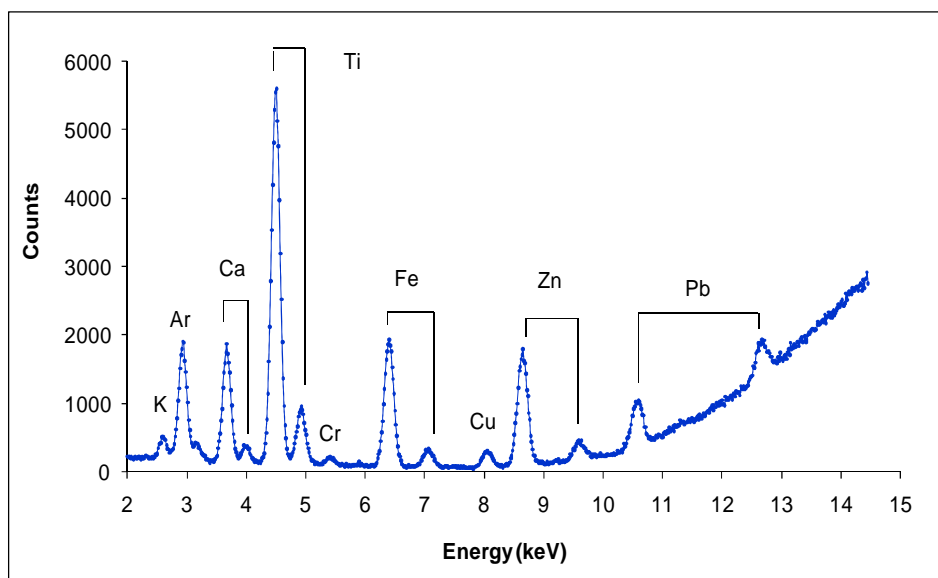


Figure 3. X-ray spectrum of the plastic garbage bag sample no. 9, showing the main peaks for the elements K, Ca, Ti, Cr, Fe, Cu, Zn and Pb (argon characteristic peaks are from the atmosphere between sample and detector).

Table 1 and Figure 4 show the K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr and Pb concentrations ($\mu\text{g g}^{-1}$) in 14 garbage bag samples. Some elements showed minimum and/or maximum concentrations well above their limits of detection. The concentration ranges for those elements were K: <LD - 240; Ca: 130 - 8900; Ti: 1002 - 8600; Cr: <LD - 63; Mn: <LD - 23; Fe: 40 - 390; Cu: 2.0 - 245; Zn: 19 - 167; Sr: <LD - 11 and Pb: <LD - 130 $\mu\text{g g}^{-1}$.

The trueness of the EDXRF technique was verified by analyzing a standard reference material produced by NIST, named "air particulate on filter media, SRM2783". The concentration of K, Ca, Ti, Mn, Fe, Cu, Zn and Pb determine by EDXRF were in close agreement with the certified values.

4. CONCLUSIONS

The proposed technique was capable of determine K to Ti at concentrations higher than 10 - 40 $\mu\text{g g}^{-1}$, and for Cr to Sr and Pb at concentrations higher than 1 - 5 $\mu\text{g g}^{-1}$ in the plastic garbage bag samples without chemical digestion, by a direct, non-destructive, multielemental and simultaneous analysis in approximately 10 min. All samples showed relative high content of Ca (130 - 8900 $\mu\text{g g}^{-1}$) and Ti (1002 - 8600), and small amount of K (<LD - 240), Mn (<LD - 23), Fe (40 - 390), Cu (2.0 - 245), Zn (19 - 167) and also Cr (<LD - 63) and Pb (<LD - 130 $\mu\text{g g}^{-1}$) harmful elements.

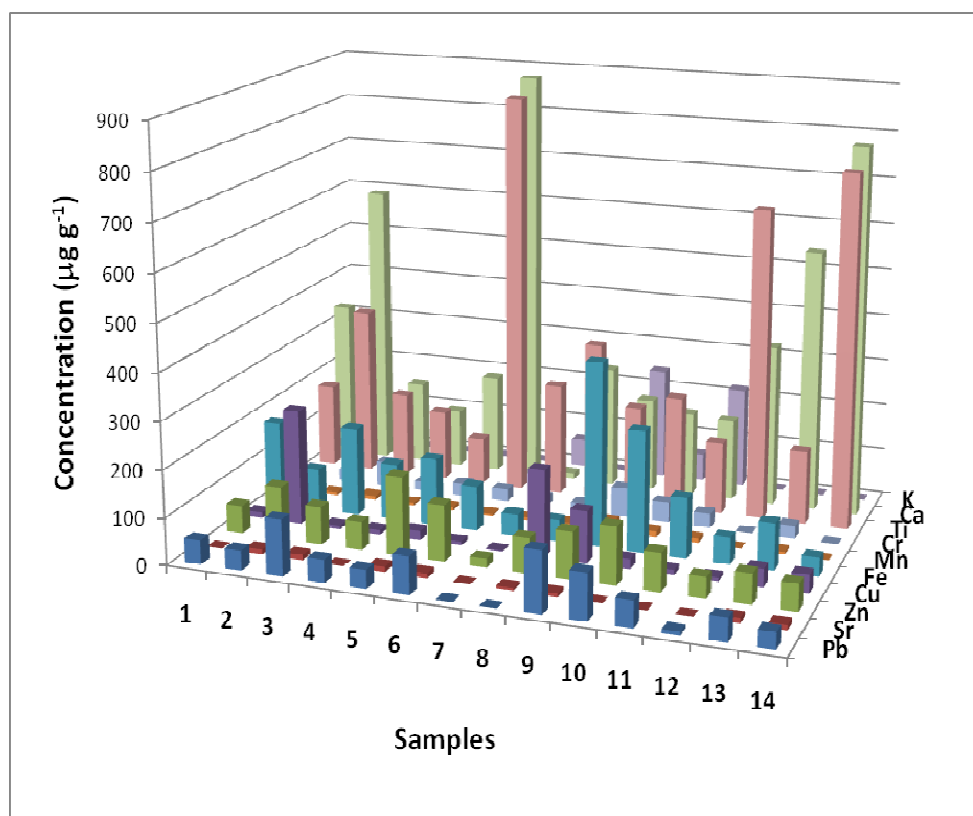


Figure 4. Concentrations ($\mu\text{g g}^{-1}$) of the elements from K to Pb in the plastic garbage bag samples (the Ca and Ti concentrations are divided by 10).

Table 1. Concentrations and limit of detection ($\mu\text{g g}^{-1}$) of the elements from K to Pb in the plastic garbage bag samples.

SAMPLE	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Sr	Pb
1	< LD	3400	1800	17	5	180	13	59	< LD	51
2	< LD	6100	3600	25	6	87	245	111	10	42
3	< LD	1780	1800	53	9	188	7	80	11	119
4	< LD	1250	1500	19	5	120	10	60	< LD	48
5	< LD	2120	1002	27	7	143	20	167	11	40
6	< LD	8900	8600	26	3	95	9	119	10	80
7	60	130	2400	19	5	47	2	19	< LD	< LD
8	< LD	2600	3400	17	6	46	184	74	5	< LD
9	240	2000	2100	63	23	390	110	100	8	130
10	59	1800	2420	44	13	258	21	123	< LD	98
11	216	1740	1540	31	10	128	11	81	< LD	56
12	< LD	3470	6630	< LD	< LD	57	8	44	< LD	7
13	< LD	5600	1570	28	5	99	39	65	11	49
14	< LD	7900	7540	< LD	< LD	40	39	57	11	34
LD	38.9	19.4	7.1	3.1	2.1	1.5	0.86	0.85	4.6	2.8

* LD = limit of detection

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