HOUSE DUST METAL DETERMINATION BY WDXRF TECHNIQUE

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ABSTRACT

In this work, an analytical procedure for the quantitative analysis of the metals determination in house dust samples by wavelength dispersive x-ray fluorescence technique (WDXRF) is described. The fundamental parameters method (FP) was applied and direct pressed powder technique was used for sample preparation.

The methodology validation and measurement uncertainty were evaluated by the EURACHEM/CITAC Guide 4715-92, statistical tests. Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Sr and Pb were determined in the standard reference materials.. The SRM data presented an uncertainty of measurement, calculated as the relative standard deviation (RSD), lower than 3% for all the elements at 0.05% significance level; except for Na, K, Ti, Ni, Se e Pb determination. These elements presented 10.9 - 3.4 – 5.4 – 5.7 – 5.0 -3.8 % RSD values, respectively. The accuracy of the method presented the Z-score values between -2<IzI2 for all elements, except to Cr, Cu, Zn, and Pb (2<IZI<3) showing the methodology application for metal determination in house dust samples. The detection and quantification limits were also determined for all the elements. The method compared to other instrumental techniques such as ICP/OES and AAS shows advantage, once the chemical treatments or complex dissolution processes are not required for samples preparation.

Key words: x-ray fluorescence, house dust analysis, methodology validation

1 Introduction

The world-wide technological advance has supplied the necessities of the human beings but at the same time produces environmental and human health problems. A great variety of chemical substances are introduced in the buildings, offices and houses, mainly from additive substances present in several products such as fibers, carpets, curtains, televisions, computers and cosmetics [1]. Research carried out about the ambient impact and human health have shown that some of these additives could escape from the products and contaminate the indoor environment during its normal use, consecutive or through wear for a time. These substances associate to hairs, human and animal epidermal cells, materials of construction, household furniture and particulate matter generate dust particles, often called as “house dust”. The correlation between house dust and diseases, especially from children exposure has been reported by world-wide researchers, which diseases such as childhood leukemia [2], developmental inhibition [3], reduction in motor skills, coordination and attention disorders [4].

Inside this context, a precise, accurate, fast and low cost characteristics analytical methodology became necessary for the evaluation of the inorganic content in house dusts studies.

In this work, a methodology using the wavelength dispersive X-ray fluorescence technique (WDXRF) with the fundamental parameters method (FP) is presented. This methodology allows fluorine (Z=9) to uranium (Z=92) determination, since percentage (%) to parts per million (mg g^{-1}) concentration level in the house dust samples.

The house dust samples were collected from 4 different zones of Sao Paulo city. The residents themselves collected the indoor dusts by vacuuming according to a protocol designed to capture surface dusts for different types of bare floors, area rugs, furniture and others.

The methodology validation was carried out through statistical tools EURACHEM/CITAC Guide 4715-92 [5] applied to the standards reference materials SRM 2781 and 1547 from NIST/USA and certificate reference material CRM N$^{\underline{0}}$ 9 from NIES/Japan.

2 Experimental

2.1 Sample preparation

The samples SRM 2781, SRM 1547 and CRM N$^{\underline{0}}$ 9 were prepared as simple pressed pellets. 2g to 3g of acid boric (H_3BO_3) were accommodated in a special steel cylindrical mold (Hidraulic press - B.Herzog, model HP40) and pressed at 5 ton (100MPa) for 1 minute, obtaining one base; after were added amounts between 0.3-0.5g of powdered sample on this base and pressed at 10 ton (203MPa) for 1 minute; thus a 20±1 mm diameter and 10±1 mm thickness pellet was obtained.

Multi-element analyses were carried out with a wavelength dispersive X-ray fluorescence spectrometer from RIGAKU Co. (model RIX 3000, Rh X-rays tube). The measurement instrumental parameters like voltage (kV), current (mA), collimators, filters, attenuator, analyze crystal, detector, 2θ positions and fixed counting time was established for each characteristic emission line, using high purity certified materials.

2.2 Instrumental Sensitivity

Instrumental sensitivity, for fundamental parameter method, is defined as the quotient between the theoretical intensity (calculated) and experimental intensity (measured). The intensity varies for each chemical element and its determination is function of the spectrometer optic system, mainly reflection efficiency of the crystal and the detector [6]. Using well-known chemical composition samples, the instrumental sensitivity is calculated for each chemical element. The sensitivity curve is obtained by relating the instrumental sensitivity and the atomic number of each element. A very accurate sensitivity curve is obtained with a great number of repetitions. The use of pure elements is preferable; however, compounds can also be used, once its chemical composition is very well-known. Through instrumental sensitivity curve, registered in a library, is possible to analyze the elements from fluorine (Z=9) to uranium (Z=92), percentage to mg g^{-1} concentrations levels [7]. The experimental instrumental sensitivity curve for the K lines emission (F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Br, Sr, Y, Zr, Nb, Mo, Pd, Ag, Cd, Sn, Sb, Te and I) and L lines (Ba, REE (rare earth elements), Pt. Au, Pb, Tl, Bi, Th and U)) was obtained from certified materials and high pure certified compounds (FIG 1) .

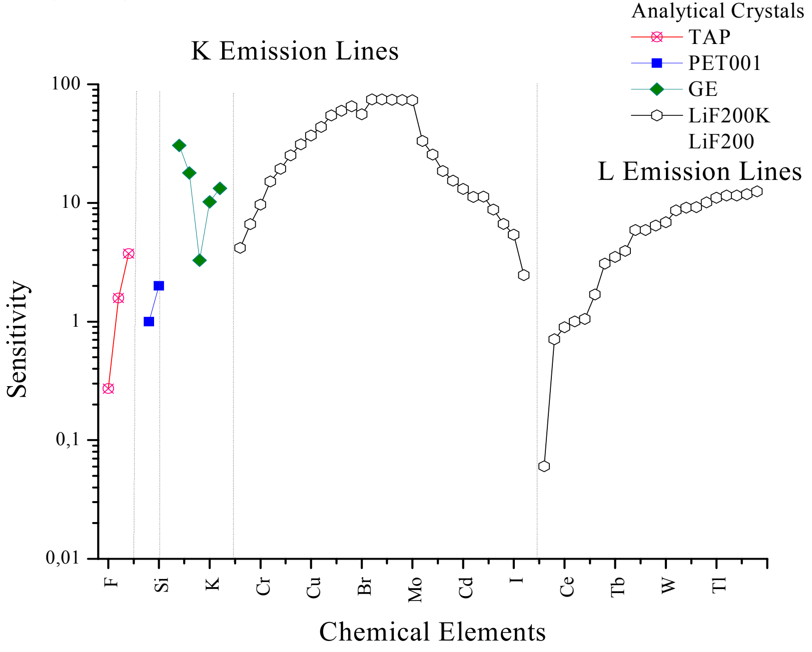

Fig. 1. Instrumental sensitivity curve for the K and L emission lines (RIGAKU Co., model RIX 3000, spectrometer)

2.3 Limit of Quantification (LOQ)

The limit of quantification, for fundamental parameter method, is correlated with instrumental sensitivity, where the continuous spectrum and the emitted characteristic lines of the elements are calculation parameters for sensitivity (*m*).

Therefore, for each emission line, there is an specific area related to the continuum spectrum and one part of the *continuum* related to the *background* intensity (BG).

Usually, the limit of quantification for each element is expressed as an elemental concentration (µg g^{-1}) , at 0.05 % significance level [8], obtained from three times background net intensity (cps), according to Eq. (1).:

$$LOQ_{\mu g g^{-1}} = \frac{3}{m} \cdot \frac{\sqrt{BG}}{T_{BG}} \tag{1}$$

where

m = sensitivity (quotient between the theoretical/experimental intensity) extracted from sensitivity curve;

BG = background intensity in the peak position, expressed in counting per second (cps);

T_{BG} = total time (measuring time at background and peak 2θ positions);

The BG intensity was calculated according to Eq (2).

$$BG = \frac{i_1(2\theta_3 - 2\theta_2) + i_3(2\theta_2 - 2\theta_1)}{2\theta_3 - 2\theta_1} \tag{2}$$

where

I_1, I_3 = background intensity, left and right from the peak, respectively.

$2\theta_2, 2\theta_1, 2\theta_3$ = Bragg angle position (2θ) in the peak, left and right, respectively.

The limit of quantification was calculated for F to U elements from experimental sensitivity curve (Fig. 1).

Table 1. The limits of quantification for F to U elements

Element	LOQ (µg g^{-1})	Element	LOQ (µg g^{-1})	Element	LOQ (µg g^{-1})
F	5	Ge	9	Nd	10
Na	5	As	10	Sm	9
Mg	5	Br	15	Gd	6
Al	5	Sr	15	Tb	5
Si	5	Y	15	Dy	6
P	5	Zr	16	Yb	6
S	5	Nb	19	Hf	7
Cl	7	Mo	21	Ta	8
K	5	Pd	36	W	8
Ca	6	Ag	37	Ir	8
Ti	15	Cd	32	Pt	10
V	10	Sn	28	Au	10
Cr	7	Sb	31	Hg	10
Mn	7	Te	31	Tl	8
Fe	7	I	32	Pb	12
Co	7	Cs	42	Bi	10

Ni	8	Ba	10	Th	15
Cu	9	La	11	U	17
Zn	13	Ce	10		
Ga	9	Pr	11		

2.4 Validation of the Methodology

The evaluation and validation of the method were verified by the SRM 2781(Domestic Sludge), SRM 1547 (Peach Leaves) and CRM N$^{\underline{0}}$ 9 (Sargasso). These materials have different chemical composition and they were prepared in three replicates and for each one twelve measurements were carried out. The results were evaluated by statistical tests, recommended by EURACHEM/CITAC Guide.

The precision of the method was evaluated according to the following steps. At first, the Chauvenet's rejection test [9] was used to eliminate outliers, according to Eq. (3). After the elimination of outliers, a new average and its standard deviations were calculated, according to Eq. (3).

$$|x_i - \bar{x}| \rangle k_{(n)} s \tag{3}$$

where

x_i = measured value;

$\bar{x}$ = arithmetic mean of the set;

$k_{(n)}$ = Chauvenet's coefficient table;

s = standard deviation of the set.

The t-Student test was applied to calculate the method precision according to Eq.(4)

$$U = \bar{X} \pm t_{n-1.\alpha/2} \frac{s}{\sqrt{n}} \tag{4}$$

where

$\bar{x}$ = arithmetic mean of the set;

$t_{n-1.\alpha/2}$ = t-Student value;

s = standard deviation of the all replicates;

n = number of the replicates.

The Z-score test was applied to calculate the method accuracy according to Eq. (5) [10]

$$z = \frac{\bar{x}_{det} - x_{cert}}{\sqrt{\sigma_{det}^2 + \sigma_{cert}^2}} \tag{5}$$

where

$\bar{x}_{det}$ = experimental mean value;

x_{cert} = certified value;

σ_{det} = experimental standard deviation;

σ_{cert} = certified standard deviation.

3 Results and discussion

The methodology validation and uncertainty of measurement were evaluated for Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Sr and Pb determination in the related standard reference materials. These different materials allowed an assessment of accuracy and precision over a wide range of concentrations, from percentage to mg g^{-1} level.

In Table 2 are presented the Na, Mg, Al, Si, P, K, Ca, Ti, Fe, Cr, Ni, Cu, Zn, Se and Pb certified and experimental values for SRM 2781. Also, the uncertainty of measurement calculated as the relative standard deviation (RSD %) and relative error (e_r %) are presented. All the elements presented a SRD value < 5.0 %; exception was observed for Na, Ti e Ni determination, which one showed 10.9 , 5.4 and 5.7 RSD values, respectively. The accuracy evaluated as relative error showed a value < 5.0 % for all the elements, except for Cr e Ni determinations, which one presented 5.4 and 6.4 values, respectively.

In Table 3 data are presented data for Mg, P, K, Ca, Al, Cl, Mn, Fe, Zn and Sr determination for SRM 1547 material. For all the determinations, the method showed a RSD value < 5.0 % and e_r value < 4.0 %.

In Table 4, the Na, Mg, P, S, Cl, K, Ca, Al, Fe and Br determination in CRM Nº 9, showed a value < 5.0 % for all the elements, except for As (7.7%) determination and the method presented e_r value < 5.0% for all the elements.

The results reveal an adequate precision for house dust analysis.

Table 2 Certified , determined , relative standard deviation (RSD %) and relative error (e_r %) values for SRM 2781 - Domestic Sludge, NIST

Element	Certified value (%)	Determined value (%)	RSD (%)	e_r (%)	Element	Certified value (μg g^{-1})	Determined value (μg g^{-1})	RSD (%)	e_r (%)
Na	0.21±0.02	0.21±0.02	10.9	2.4	Cr	202±9	213±4	2.5	5.4
Mg	0.59±0.04	0.57±0.01	2.5	2.9	Ni	80.2±2.3	85.3±3.2	5.7	6.4
Al	1.6.0±0.1	1.60±0.03	2.4	0.3	Cu	627±13	639.1±1.3	0.3	1.9
Si	5.1±0.2	5.0±0.1	2.5	1.7	Zn	1273±53	1296±4	0.4	1.8
P	2.42±0.09	2.39±0.03	2.0	1.4	Se	16.0±1.6	16.6±0.6	5.0	3.8
K	0.49±0.03	0.51±0.01	3.4	4.5	Pb	202.1±6.5	211.3±5.3	3.8	4.6
Ca	3.9±0.1	4.0±0.1	2.7	1.7					
Ti	0.32±0.03	0.31±0.01	5.4	2.7					
Fe	2.8±0.1	2.9±0.1	2.8	4.1					

Table 3 Certified , determined , relative standard deviation (RSD %) and relative error (e_r %) values for SRM 1547- Peach Leaves, NIST

Element	Certified value (%)	Determined value (%)	RSD (%)	e_r (%)	Element	Certified value (μg g^{-1})	Determined value (μg g^{-1})	RSD (%)	e_r (%)
Mg	0.432±0.008	0.444±0.023	4.2	2.7	Al	249±8	247±2	0.7	0.7
P	0.137±0.007	0.132±0.023	1.7	3.8	Cl	360±19	363±2	0.4	0.7
K	2.43±0.03	2.45±0.05	1.5	0.9	Mn	98±3	98±1	1.0	0.2
Ca	1.56±0.02	1.61±0.02	1.0	2.9	Fe	218±14	224±4	1.6	2.7
					Zn	17.9±0,4	18,4±0,4	1.7	2.8
					Sr	53±4	55±1	1.9	3.1

Table 4 Certified , determined , relative standard deviation (RSD %) and relative error (e_r %) values for CRM N$^{\underline{0}}$ 9 – Sargasso, NIES

Element	Certified value (%)	Determined value (%)	RSD (%)	e_r (%)	Element	Certified value (μg g^{-1})	Determined value (μg g^{-1})	RSD (%)	e_r (%)
Na	1.70±0.08	1.75±0.20	4.6	3.0	Al*	215	217±25	-	1.0
Mg	0.65±0.03	0.64±0.11	4.7	1.0	Fe	187±6	180±20	3.3	4.0
P	0.260±0.003	0.27±0.03	1.1	2.0	As	115±9	117±13	7.7	2.0

S	1.2±0.1	1.2±0.1	4,1	2,0	Br*	270	275±30	-	2.0
Cl	5.1±0.2	5.2±0.6	3.8	2.0					
K	6.10±0,20	6.06±0.68	3.3	1.0					
Ca	1.34±0.05	1.35±0.20	3.7	1.0					

*Estimated value

Moreover, the Z-score values were calculated for the Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Sr and Pb determination to evaluate the accuracy of the method according to *ISO 17025: 2005*. The values IZI ≤ 2 are considered satisfactory, 2 < IZI ≤ 3 values are questionable and IZI > 3 are considered unsatisfactory.

The experimental Z-score values for SRM 2781, SRM 1547 and CRM Nº 9 materials are presented in Figure 2. The Na, Mg, Ag. Si, P, K, Ca, Ti, Fe, Ni, Se and Pb determination presented IZI values ≤ 2, exception was observed for Cr, Cu, Zn and Pb determination in the SRM 2581 material, tshowing 2.5, 2.4, 2.6 and 2.4 values, respectively. Therefore, a better measurement condition should be established for these elements determination.

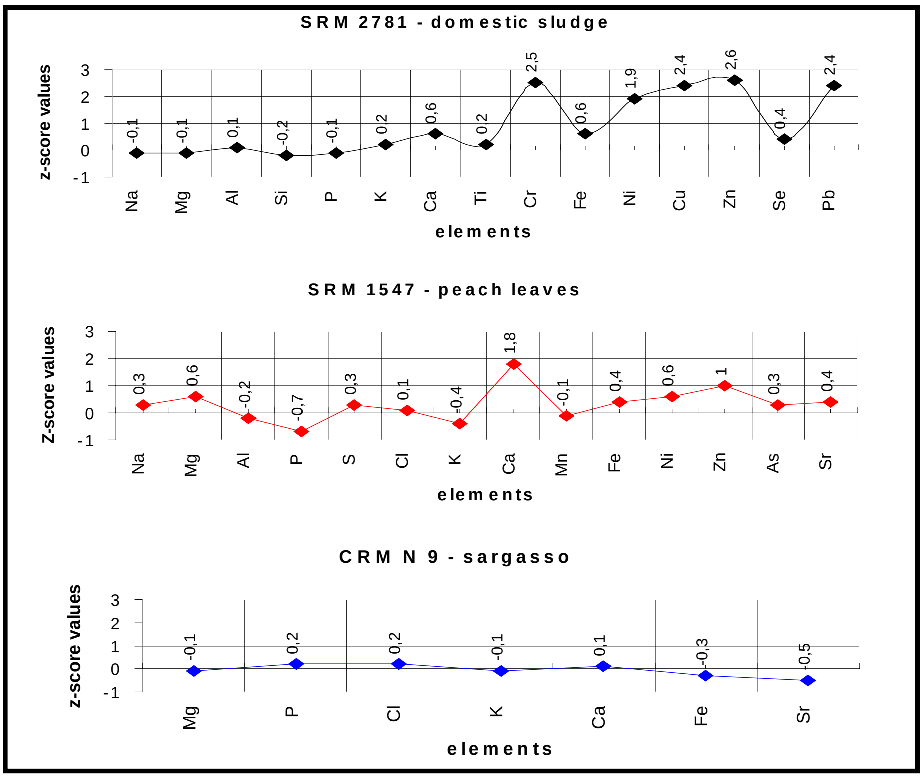

Fig. 2. Z-score values for SRM 2781, SRM 1547 and CRM N$^{\underline{0}}$ 9 reference materials

4 Conclusions

The methodology allows the inorganic elements determination since percentage to mg g^{-1} concentrations in different material such as leaves, dust house and algae. The method is rapid, simple and shows adequate accuracy and precision for this kind of analysis. The procedure was valid for Na, Mg, Al, P, S, Cl, K, Ca, Fe, Ni, Zn, As and Sr quantitative determination in the house dust samples.

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