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EVALUATION OF THE WOOD CCA PRESERVATIVE TREATMENT PROCESS OF EUCALIPTUS (*Eucaliptus ssp*) BY X-RAY FLUORESCENCE TECHNIQUE

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ABSTRACT

Brazil produces around 1,2 mi m³ of treated wood to meet the annual demand of railway, electric, rural and construction sectors. The treated woods used for poles, sleepers, fence posts and plywoods should be according to Brazilian norms requirements. The most used wood species are eucalyptus (*Eucaliptus ssp)* and pine (*Pinus ssp*).

The most wood preservative products used in Brazil are CCA (chromated copper arsenate) and CCB (copper chromium and boron salt). The analytical methods, such as Flame Atomic Absorption Spectrometry (FAAS) and Plasma Inductively Coupled Optical Emission Spectrometry (ICPOES) have been used for the evaluation of those treatment processes.

In this work, the sapwood sample was obtained from eucalyptus trees (*Eucaliptus ssp*) obtained from Minas Gerais State, Brazil, cut plantation areas. Sawdust sapwood sample was grounded and submitted to different additions of CCA solutions (0.2, 0.7, 1.3, 2.3, 3.6, 6.3, 11.7 and 17.9 kg m^{-3}). Power and pressed pellets sapwood samples, analyzed by EDXRFS, showed a good linear relation ($r^2 > 0.99$) between the characteristic intensity fluorescent lines (CuKα, CrKα and AsKß) and their concentration, also, showed adequate sensitivity (LQ < 5 mg kg^{-1}) for Cu, Cr and As determination in treated woods. Cu, Cr and As were determined in powdered sawdust samples by FAA spectrometry, using the AWPA A11-93 standard method; the relation between the CCA retention and their concentration showed a lower linear relation than EDXRFS; the FAAS spreading result could be attributed to laboratorial CCA addition process.

1. INTRODUCTION

Brazil is a privileged country concerning the diversity of wood species, from its great natural forests. However, the exploitation of native species by predatory and illegal ways, is leading to a perspective of disappearance of almost 20% of the Amazon region forest coverage in less than 50 years away[1]. According to the Associação Brasileira de Produtores de Florestas Plantadas (ABRAF), in 2009, the production of forest wood in log form, from eucalyptus and pine, reached an amount estimated of 250.3 mi m^3 year. Brazil produces around 1.2 mi m³ of treated wood to meet the annual demand of railway, electric, rural and construction sectors. The most used wood species are eucalyptus (Eucaliptus ssp – 73%) and pine (Pinus ssp – 27%). The treated wood, used for poles, sleepers, fence posts and wooden construction, should be according to the requirements of Brazilian norms[2].

With versatility and easy handle associated to its mechanical properties, wood is a type of material comparable to steel, concrete and polymeric materials as to its different applications. Due to organic matter, wood has its durability affected by xylophages' agents, such as fungi, termites and wood borers.

The wood preservative treatment, such as chemical treatment, thermal treatment, biological control and thermal wood modification, aims to increase its natural durability.

In Brazil, the regulated wood preservative products are CCA (chromated copper arsenate), CCB (copper chromium and boron salt) and CA-B (copper azole type B). Analytical techniques, such as Flame Atomic Absorption Spectrometry (FAAS) and Plasma Inductively Coupled Optical Emission Spectrometry (ICPOES) have been used for the evaluation of wood preservative treatment processes.

X-ray fluorescence spectrometry[3,4,5] has developed into a well-established multi-elemental analytical technique, with a wide field of practical application in mineralogy, biology, archeology and forensic areas. The technique is a nondestructive, fast, precise and low-priced method, compared to other analytical techniques such as FAAS and ICPOES[6].

The application of X-ray fluorescence spectrometry (EDXRF: energy dispersive X-ray fluorescence and PXRF: portable X-ray fluorescence) have been strongly recommended in wood treatment control process and wood waste assortment by Forest Products Industry Technology Roadmap[7].

In this work, Cu, Cr and As were determined in treated sawdust sapwood sample by EDXRF technique, using the Fundamental Parameters method[8] and the same elements were determined by FAAS, using the AWPA A11-93 standard method[9].

2. METHODS

2.1. Sampling

The wood sample was obtained from eucalyptus trees (*Eucaliptus ssp*) of Minas Gerais State, Brazil, cut plantation area; and the sawdust sample was obtained from the sapwood tree.

2.2. Sample preparation

The sapwood tree was prepared in a Willey-mill grinder until reaching 120 mesh sawdust powders. Then, the powder was dried in an oven at 103 ± 2 ºC, obtaining a constant mass. Different concentrations of CCA solutions were added in order to obtain different retentions (0.2, 0.7, 1.3, 2.3, 3.6, 6.3, 11.7 and 17.9 kg of CCA in m^{-3} wood).

2.3. FAAS analysis

The Cu, Cr and As, in treated powder sawdust samples, were determined using the AWPA A11-93 method (Standard Method for Analysis of Treated Wood and Treating Solutions by Flame Atomic Absorption Spectroscopy[9]) and performed in a VARIAN, model SpectrAA 200, FAA spectrometer. The measurement conditions are shown in Table 1.

Table 1: Measurement conditions at FAA spectrometer from VARIAN, model SpectrAA 200

Element	Wave length light (nm)	Flame	Standard solutions range* (mg l^{-1})
Cu	324.8	Air-Acetylene	5 – 20
Cr	357.9	Air-Acetylene	5 - 20
As	193.7	Air-Acetylene	25 - 100

* Standard solution concentration range for individual calibration curve

2.4. EDXRF analysis

The treated sawdust samples were analyzed in powder and pressed pellets forms; these were prepared in 2.0 cm diameter double layer pellets, using B. HERZOG, model HTP40 hydraulic press. The natural sawdust sample, *i.e*. without CCA addition, was also prepared in both forms. The EDXRF analysis was carried out in a SHIMADZU Co. model Rany, spectrometer, using the Fundamental Parameters method. The measurement conditions are shown in Table 2.

Table 2: Measurement conditions at EDXRF spectrometer from SHIMADZU Co., model Rany

Parameter	Conditions
X ray tube	Rh target
Voltage	40 kV
Current	Adjustable (100 μA maximum)
Detector	Si(Li)
Atmosphere	Vacuum
Collimator	5mm
Fixed count time	100 seconds
Emission line	$K\alpha$ to all elements and K_β to As

3. RESULTS AND DISCUSIONS

In Table 3, the elemental composition of natural sapwood of *Eucalyptus ssp* tree, determined in powder and pressed pellets samples, is presented. The mean $\pm 1\sigma$ concentration for Ca, K, Mg, Al, S, P, Mn, Fe, Cu, As, Cr, Zn and Ti elements was determined, since both samples presented values statistically equal. The major elements present in *Eucalyptus ssp* sapwood are K and Ca (786 to 902 mg kg^{-1}), followed by Mg, Al, and S (104 to 274 mg kg^{-1}); P, Mn, Fe, Cu, As, Cr, Zn and Ti elements are present in trace level (< 50 mg kg^{-1}). Cu and As are present in natural sapwood in trace level, 15±3 and 10±2 mg kg^{-1}, respectively.
The linear correlation between any analytical signal and its concentration leads to minor errors in the accuracy assessment and it is, also, the best form to evaluate the repeatability and reproducibility of the analytical method. Therefore, the CCA solution addition process, in sawdust powder, was assessed by the Cu, Cr and As elemental concentration in relation to

their characteristic fluorescent intensity (CuK_{α}, CrK_{α} and AsK_{β}), as shown in Figure 1. The results showed that the entire process involving the grinding, CCA addition, drying and homogenization steps are reproducible; the correlation coefficients (r^2) showed to be > 0.99 (Cu: 0.999 and 0.998, Cr: 0.999 and 0.999 and As: 0.998 and 0.996 for the powder and pressed pellets samples, respectively).

Also, the CCA addition process in sapwood was evaluated by the linear relation between Cu, Cr and As elemental concentration and CCA retentions (kg m^{-3}), calculated by FAAS analysis. The results showed the correlation coefficients (r^2) ≥ 0.99 (Cu: 0.996 and 0.992, Cr: 0.998 and 0.990 and As: 0.996 and 0.994, for the powder and pressed pellets samples, respectively), presenting reproducibility of the CCA addition process (Fig. 2). Likewise, the CCA retentions were related to Cu, Cr and As elemental concentrations, determined by FAAS (Figure 3). The results showed the coefficient correlation values (r^2) 0.946 for Cu, 0.938 for Cr and 0.965 for As. The spread of Cu, Cr and As values can be attributed to CCA different impregnation rate in sapwood, by complexation and crosslinking phenomena that contributed to a different Cu, Cr and As extraction rate, for FAAS analysis.

The accuracy evaluation of the method for Cu, Cr and As determination in treated wood is difficult, since certified reference materials of CCA treated wood are not available in the national and international market. In this work, the CCA treated sapwood control sample has been prepared for future accuracy evaluation.

The AWPA A11-93 method, this time, has not been available to support adequate precision and accuracy evaluation, and further studies are recommended.

The AWPA A09-12 method (Standard method for analysis of treated wood and the treatment of solutions by X-ray spectroscopy[10]) has provided some guidance for the accurate evaluation, but only the repeatability and reproducibility evaluation have been listed. In same norm is related the lack of certificated reference materials and the difficulty for the accuracy assessment.

Table 3: Chemical composition of *Eucaliptus ssp* natural sapwood determined by EDXRF spectrometry

Element	Concentration mg kg^{-1}		
	Powder sample	Pressed pellet sample	Mean ±1σ
K	794	1010	902 ± 108
Ca	716	857	786 ± 71
Mg	262	231	247 ± 15
Al	235	273	254 ± 19
S	73	134	104 ± 30
P	37	46	42 ± 5
Mn	35	34	34 ± 2
Fe	20	54	37 ± 17
Cu	17.9	11.9	15 ± 3
As	10.8	8.2	10 ± 2
Cr	7.65	20.0	13 ± 5
Zn	3.70	5.6	5 ± 2
Ti	3.21	2.9	3 ± 1

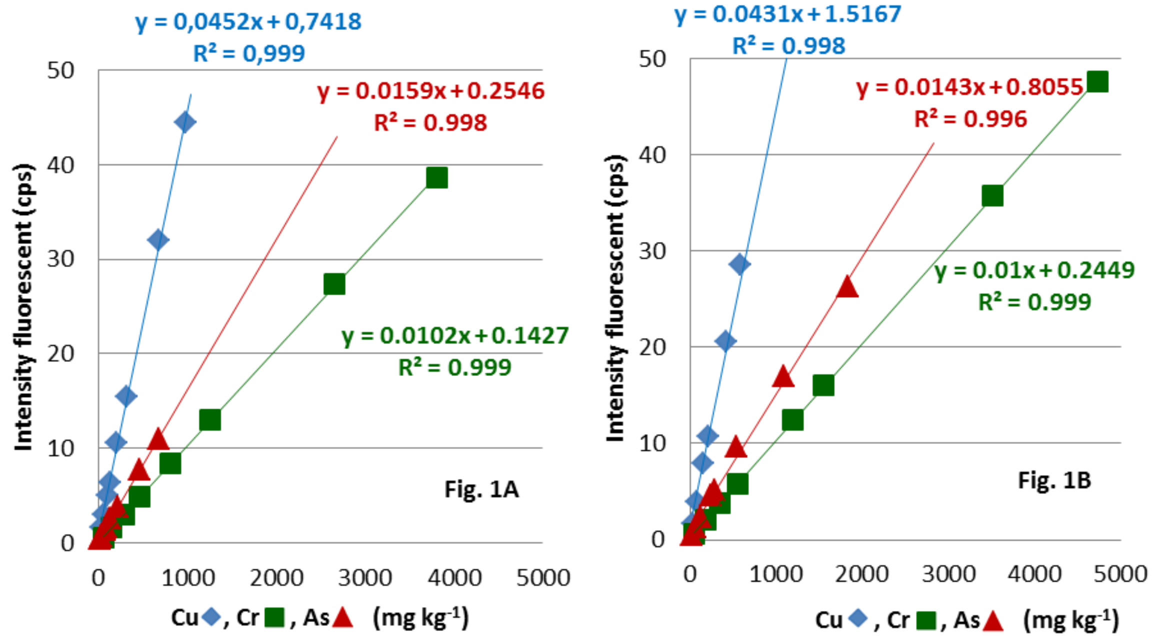

Figure 1: Cu, Cr and As elemental concentration (determined by EDXRFS) in relation to characteristic fluorescence intensity (CuKα, CrKα and AsKβ), in the powder (Fig. 1A) and pressed pellets (Fig 1B) samples.

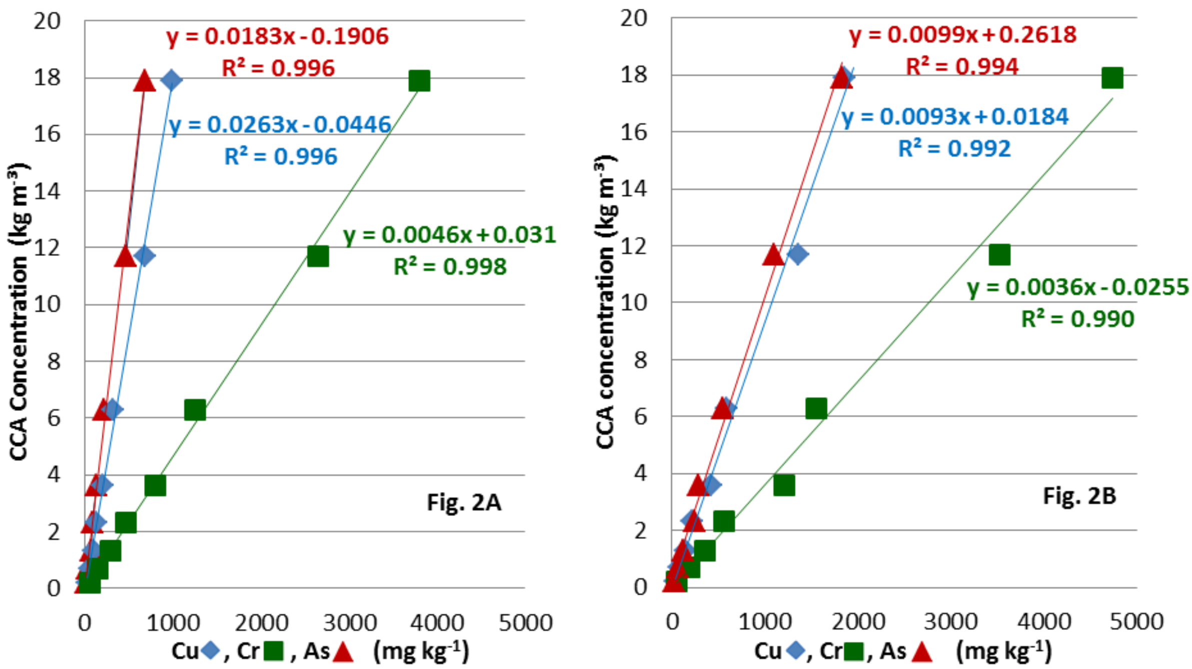

Figure 2: Cu, Cr and As elemental concentration (determined by EDXRF) in relation to CCA retention, in powder (Fig. 2A) and pressed pellets (Fig 2B) samples.

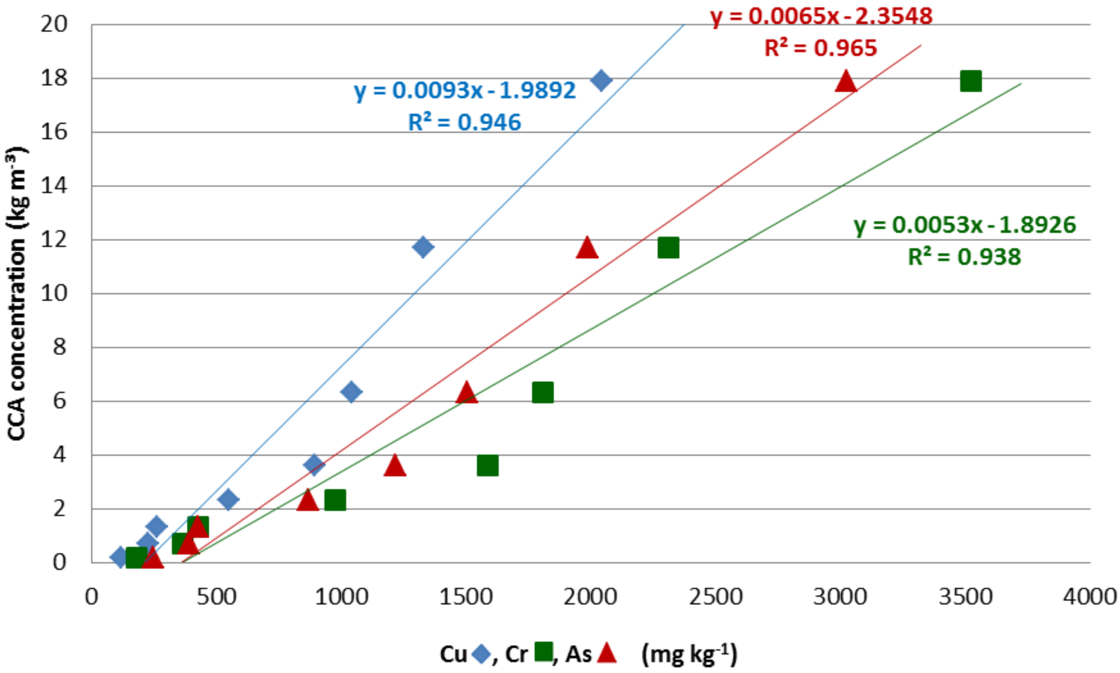

Figure 3: Cu, Cr and As elemental concentration (determined by FAAS) in relation to CCA retention in powder samples.

4. CONCLUSIONS

In this work, FAA and EDXRF spectrometries were used to Cu, Cr and As determination, in *Eucaliptus ssp* specie treated wood samples.

The AWPA A03-93 standard method, using FAA spectrometry, showed adequate reproducibility and sensibility. The use of certified standard solutions and standardized methods resulted in traceability and confidence results. However, the method is a destructive analysis, requires the sample preparation, use of chemical reagents and performed mono-elemental determination, leading to costly analysis, besides producing chemical waste.

The EDXRF spectrometry, using the Fundamentals Parameters method, showed good sensitivity and reproducibility for Cu, Cr and As determination, in CCA preserved wood. The advantages of this method are based on the multi-elemental determination, not requiring individual calibration curves, easy sample preparation plus fast and low-priced analysis and it does not produce chemical waste.

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REFERENCES

1. G. J. Zenid et al., *Madeira: Uso Sustentável na Construção Civil*. Instituto de Pesquisas Tecnológicas, São Paulo, Brasil (2009).
2. Norm ABNT NBR 16143:2013 – *Preservação de Madeiras – Sistema de Categorias de Uso* (2013).
3. K. Tsuji, J. Injuk, R. V. Grieken. *X-ray fluorescence spectrometry. Recent Technological Advances.*, John Wiley & Sons, Chichester, England (2004).
4. B. Beckhof, B. Kanngießer, N. Langhoff, R. Wedell, H. Wolff. *Handbook of practical x-ray fluorescence analysis*, Springer, Berlin-Germany (2006).
5. P. J. Potts, M. West *Portable X-ray Fluorescence Spectrometry Capabilities for In Situ Analysis*, RSC Publishing, Cambridge, England (2008)
6. I. M. Sato; L.A.T. Pereira, M.A. Scapin, M.B. Cotrim, C.S. Mucsi, J.L. Rossi; L.G. Martinez. "Chemical Anal Microestructural characterization of Remelted Zircaloy by Z-ray fluorescence techniques and metallographic analysis," *J. Radioanal. Nucl. Chem.*, **V. 249**, pp. 283–288 (2012).
7. Agenda 2020 Technology Alliance, U.S. Department of Energy, American Forest & Paper Association Georgia Institute of Technology, *Forest Products Industry Technology Roadmap*, Georgia, United States of America (2010).
8. G. R. Lachance, F. Claisse, *Quantitative x-ray fluorescence analysis. Theory and application*. John Wiley & Sons, Chichester, England (1995).
9. AMERICAN WOOD-PRESERVERS' ASSOCIATION (AWPA), *AWPA Book of Standards 2007*: Method A11-93 Standard Method for Analysis of Treated Wood and Treating Solutions by Atomic Absorption Spectroscopy, Birmingham, Alabama United States of America, (2007).
10. AMERICAN WOOD-PRESERVERS' ASSOCIATION (AWPA), *AWPA Book of Standards 2012*: Method A09-12 Standard method for analysis of treated wood and treating solutions by X-ray spectroscopy, Birmingham, Alabama United States of America, (2012).