

# Determination of Cu, Cr, and As in preserved wood (*Eucalyptus* sp.) using x-ray fluorescent spectrometry techniques

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**Abstract** Energy dispersive (EDXRF) and Portable (PXRF) X-ray fluorescence techniques are proposed for wood treatment control process and wood waste assortment. In this study, different retentions of chromated copper arsenate preservative were applied to *Eucalyptus* sp. sapwood samples. Cu, Cr and As were determined by XRF techniques in treated sapwood massive blocks and treated sapwood sawdust samples were analyzed by FAAS spectrometry (Flame Atomic Absorption) and INAA (Instrumental Neutron Activation Analysis). Cu, Cr and As mean values, obtained by FAAS and INAA, showed to be statically equal; however, XRF analysis showed considerable deviations, presenting the absorption and the enhancement effects in analytical lines.

**Keywords** Preserved wood · *Eucalyptus* sp. · X-ray fluorescence techniques · Instrumental neutron activation analysis · Flame atomic absorption spectrometry

## Introduction

The Brazilian annual demand for treated wood is around 1.2 mi m<sup>3</sup> to meet the railway, electric, rural and construction sectors. The most used wood species are eucalyptus (*Eucalyptus* sp.), 73 %, and pine (*Pinus* sp.), 27 %. According to the Brazilian Association of Forest Plantation Producers (ABRAF) [1], in 2009, the production of the forest wood in log form, from eucalyptus and pine, reached an amount estimated of 250.3 thousand m<sup>3</sup> year.

Wood chemical treatment is necessary due to its organic matter, since xylophage agents, such as fungi, termites and wood borers, affect its durability. The treated wood, used for poles, sleepers, fence posts and wooden construction should be in accordance with the Brazilian norms [2]. The most used preservative products are CCA (chromated copper arsenate), CCB (copper chromium and boron salt) and CA-B (copper azole, type B).

Usually, the analytical control of wood preservative processes is outlined by flame atomic absorption spectrometry (FAAS). Nevertheless, X-ray fluorescence techniques (EDXRF: Energy dispersive X-ray fluorescence and PXRF: Portable X-ray fluorescence) are strongly recommended for the wooden sector by the USA-Forest Products Industry Technology Roadmap [3]. The Agenda proposed the implantation of XRF techniques in wood treatment analytical control and wood waste assortment (in situ analysis) activities by 2020.

XRF is a multielemental, nondestructive, fast, precise and low-priced analytical technique and it has been applied for chemical characterization in different matrices such as metallurgical, geological, biological, archeological and forensic materials [4, 5]. In recent years, PXRF has developed very rapidly due to advances in miniaturization and semiconductor detector technologies, offering some unique advantages such as in situ determinations and

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providing immediate information on the chemical composition for analysts [5].

Even though XRF analyses present high precision (high repeatability), the accuracy of the results can be affected from systematic errors produced by matrix effects, mainly the absorption and the enhancement effects; therefore the use of certified reference materials is of vital importance for methodology evaluation.

PXRF is mostly used for qualitative analysis. Solo-Gabriele et al. [6] used PXRF and laser induced breakdown spectroscopy (LIBS) for qualitative identification between CCA and CCB preservatives in treated wood. Authors, such as Jacobi et al. [7, 8], have used PXRF in wood assortment. Block et al. [9] related the precision and accuracy for As determination in treated wood; they also discuss the difference of As concentration determined by AAS and by PXRF and they proposed matrix correction, using reference materials. Authors, such as Hou et al. [10] and Kalnicky and Singhvi [11] have related the certified reference materials unavailability for accuracy evaluation and endorse the necessity of standard materials, with known composition, for the correction of the absorption and enhancement phenomena. Cu, Cr and As determination by XRF techniques is still under research and there is no reference in the literature, regarding their simultaneous determination in preserved woods by XRF techniques.

So far, the A09-12 XRF method [12] of the American Wood Protection Agency (AWPA) provides some support for repeatability and reproducibility evaluation. It also reports the accuracy evaluation difficulty, due to lack of certified reference materials.

Instrumental Neutron Activation Analysis (INAA) has been used for the determination of elements in several matrices, due to its high specificity and its few sources of bias in common with non-nuclear techniques. INAA has been, extensively, used for the certification of elements in geological and biological reference materials [13, 14]. Therefore, the INAA data could be used to support FAAS and XRF results in treated wood samples.

In this study, Cu, Cr and As were determined by EDXRF and PXRF using the Fundamental Parameters method [15] in treated sapwood massive block samples. FAAS and INAA techniques were used for the determination of those elements in treated sapwood sawdust

samples. XRF techniques evaluation was performed by the comparison of results.

## Experimental

### Sample collection and preparation

Eucalyptus tree wood was obtained from a plantation area at Minas Gerais State, Brazil.

In the wood treatment process, varied retentions of preservative product are required for different demands such as logs, fences and railways. *Eucalyptus* sp. sapwood samples, with the dimensions 3.0 cm × 3.0 cm × 3.0 cm (width × length × thickness, respectively) were obtained and five different concentrations of CCA preservative solutions were applied under pressure in an autoclave, in order to obtain different retentions (4.0, 6.5, 9.6, 12.8, and 16.0 kg of CCA m<sup>-3</sup> sapwood).

The biological nature of wood, mainly its anatomy variation, density and different content of cellulose, lignin and moisture, causes distinct CCA retentions [9, 16, 17]. Therefore, the retention process produces different values as to *expected* and *actual* retentions. The *actual* retentions were calculated considering block sapwood density variance, using the Method A3-08: Standard Method for Determining Penetration from AWPA [18].

From the treated sapwood samples, massive cylinder samples (approximately 2 cm length × 2 cm diameter) were obtained for EDXRF and PXRF analyses. From the same treated sapwood samples, the sawdust samples (120 mesh powder, grinded in a Willey mill grinder) were obtained for FAAS and INAA analyses.

### FAAS analysis

Cu, Cr and As determination, in treated sapwood sawdust samples, was performed by FAAS spectrometer (Varian Inc., Palo Alto, California, SpectrAA 200 model), using AWPA A11-93 method [19], with the individual calibration curve. Standard samples were prepared with individual certified standard solutions from Merck. The equipment was calibrated with standard solutions, according to the AWPA standard method, referred above. Three repetitions

**Table 1** Measurement conditions at a Varian, SpectrAA 200 model, FAAS spectrometer

Element	Wavelength (nm)	Flame	Standard solutions range <sup>a</sup> (mg L <sup>-1</sup> )
Cu	324.8	Air-Acetylene	5–20
Cr	357.9	Air-Acetylene	5–20
As	193.7	Air-Acetylene	25–100

<sup>a</sup> Concentration range for individual calibration curve

**Table 2** Measurement conditions at a Shimadzu Co., Rany 720 model, EDXRF spectrometer

Parameters	Conditions
X-ray tube	Rh
Voltage	15–40 kV (adjustable)
Tension	100–1000 μA (adjustable)
Detector	Si (Li)
Atmosphere	Vacuum
Collimator	10 mm
Fixed counting time	100 s
Irradiated area	78 mm <sup>2</sup>
Emission line	CuKα, CrKα, AsKβ

Si(Li) detector calibration: 0–20 and 0–40 keV intervals with aluminum metallic standard sample

**Table 3** Measurement conditions at a Innov-X, alpha model, PXRF spectrometer

Parameters	Conditions
X-ray tube	Ag
Voltage	15–40 kV (adjustable)
Tension	10–50 μA (adjustable)
Detector	SDD <sup>a</sup>
Atmosphere	Air
Fixed counting time	100 s
Irradiated area	78 mm <sup>2</sup>
Emission line	CuKα, CrKα, AsKα

<sup>a</sup> Silicon Drift Detector, calibrated by aluminum metallic standard sample from Innov-X

of measurements were performed; the measurement conditions are shown in Table 1.

**INAA analysis**

INAA analysis applying the comparative method was used to determine As, Cr and Cu concentration in treated sapwood sawdust samples.

As, Cr and Cu standard solutions were prepared with appropriate dilutions from Spex monoelemental standard solutions. Aliquots (50 μL) were pipetted on Whatman 40 filter paper and dried. After drying, filter papers were transferred to clean polyethylene bags.

About 50 to 100 mg of treated sapwood sawdust samples and 200 mg of reference materials (NIST SRM 1577b Bovine Liver; Fine Fly Ash CTA-FFA-1 (Institute of Polish Nuclear Chemistry and Technology, Poland and NIST SRM 2702Marine Sediment), plus standard elemental samples, were irradiated at the pneumatic system of the nuclear research reactor IEA-R1 at IPEN-CNEN/SP

**Table 4** Cu, Cr and As concentration (mg kg<sup>-1</sup>) determined by FAAS, INAA, EDXRF and PXRF (mean values and standard deviations for n = 3)

Determined retention (kg m <sup>-3</sup> )	Cu				Cr				As			
	FAAS	INAA	EDXRF	PXRF	FAAS	INAA	EDXRF	PXRF	FAAS	INAA	EDXRF	PXRF
3.9	748 ± 2	779 ± 54	599 ± 47	491 ± 13	2600 ± 4	2396 ± 243	2010 ± 165	3439 ± 67	1720 ± 10	1880 ± 50	555 ± 23	2141 ± 5
%RSD	0.3	6.7	7.8	2.6	0.2	10.1	8.2	2.0	0.6	2.7	5.2	0.2
6.7	1215 ± 3	1157 ± 64	1055 ± 81	869 ± 15	3302 ± 13	2980 ± 273	3218 ± 277	4830 ± 56	2412 ± 16	2524 ± 52	953 ± 32	3473 ± 25
%RSD	0.3	5.5	7.7	1.7	0.4	9.2	8.6	1.2	0.7	2.1	3.4	0.7
9.1	1765 ± 1	1702 ± 303	2166 ± 116	1823 ± 28	4519 ± 21	4787 ± 330	4724 ± 372	8163 ± 252	3368 ± 8	3840 ± 179	1744 ± 42	5764 ± 48
%RSD	<0.1	17.8	5.3	1.5	0.4	6.9	1.4	3.1	0.8	4.7	2.4	<1.0
12.5	2194 ± 10	2694 ± 482	2908 ± 216	2503 ± 26	5766 ± 11	6411 ± 376	6594 ± 419	11,188 ± 302	4334 ± 20	5230 ± 246	2611 ± 68	8245 ± 75
%RSD	0.4	17.9	7.4	1.0	0.2	5.9	6.3	2.7	0.1	4.7	2.6	1.0
14.0	2848 ± 12	3602 ± 421	3849 ± 272	2948 ± 38	7267 ± 13	5976 ± 358	8176 ± 274	14,533 ± 75	5754 ± 16	6111 ± 151	3205 ± 24	9417 ± 138
%RSD	0.4	11.7	7.1	1.2	0.2	6.0	3.4	5.1	0.3	2.5	7.5	1.5

%RSD relative standard deviation [20]

**Table 5** Comparison of Cu, Cr and As mean values, determined by FAAS and INAA, mg kg<sup>-1</sup>

Determined retention (kg m <sup>-3</sup> )	Cu		Cr		As	
	FAAS	INAA	FAAS	INAA	FAAS	INAA
3,9	748 ± 2	799 ± 54	2600 ± 4	2396 ± 243	1720 ± 10	1880 ± 50
<i>t<sub>exp</sub></i>	1.63		1.47		5.47	
6,7	1215 ± 3	1157 ± 64	3302 ± 13	2980 ± 273	2412 ± 16	2524 ± 52
<i>t<sub>exp</sub></i>	1.57		2.04		3.57	
9.1	1765 ± 1	1702 ± 303	4519 ± 21	4787 ± 330	3368 ± 8	3840 ± 179
<i>t<sub>exp</sub></i>	4.04		1.59		2.93	
12.5	2194 ± 10	2694 ± 482	5766 ± 11	6411 ± 376	4334 ± 20	5230 ± 246
<i>t<sub>exp</sub></i>	1.80		2.97		6.29	
14.0	2848 ± 12	3602 ± 421	7267 ± 13	5976 ± 358	5754 ± 16	6111 ± 151
<i>t<sub>exp</sub></i>	3.10		6.24		4.07	

*t<sub>crit</sub>* ( $\alpha = 0.05$ ) = 6.31

**Table 6** Comparison of Cu, Cr and As mean values, determined by FAAS, EDXRF and PXRF, mg kg<sup>-1</sup>

Determined retention (kg cm <sup>-3</sup> )	Cu			Cr			As		
	FAAS	EDXRF	PXRF	FAAS	EDXRF	PXRF	FAAS	EDXRF	PXRF
3.9	748 ± 2	599 ± 47	481 ± 13	2600 ± 4	2010 ± 165	3439 ± 67	1720 ± 10	555 ± 23	2141 ± 5
<i>t<sub>exp</sub></i>		5.49	33.84		6.19	8.80		≫6.31	≫6.31
6.7	1215 ± 3	1055 ± 81	869 ± 15	2302 ± 3	3218 ± 277	4830 ± 56	2412 ± 16	953 ± 32	3473 ± 25
<i>t<sub>exp</sub></i>		3.42	39.18		0.53	9.55		≫6.31	≫6.31
9.1	1765 ± 1	2166 ± 116	1823 ± 28	4519 ± 21	4724 ± 372	8163 ± 252	3368 ± 8	1744 ± 42	5764 ± 48
<i>t<sub>exp</sub></i>		5.99	3.59		0.95	16.94		≫6.31	≫6.31
12.5	2194 ± 9	2908 ± 216	2503 ± 26	5766 ± 11	6594 ± 419	11,188 ± 302	4334 ± 7	2611 ± 68	8245 ± 75
<i>t<sub>exp</sub></i>		5.72	19.45		3.42	22.41		≫6.31	≫6.31
14.0	2848 ± 12	3283 ± 120	2948 ± 38	7267 ± 13	8176 ± 274	14,533 ± 75	5754 ± 16	3205 ± 24	9417 ± 138
<i>t<sub>exp</sub></i>		6.25	4.35		5.74	45.88		≫6.31	≫6.31

*t<sub>crit</sub>* ( $\alpha = 0.05$ ) = 6.31

(Nuclear Research Institute, São Paulo, Brazil). For Cu determination, a  $1.0 \times 10^{12}$  cm<sup>-2</sup> s<sup>-1</sup> thermal neutron flux with 20 s of irradiation was used; a  $4.5 \times 10^{12}$  cm<sup>-2</sup> s<sup>-1</sup> thermal neutron flux with 8 h of irradiation was used for As and Cr determination.

After appropriate decay periods,  $\gamma$ -ray spectra were measured with a Ge detector POP TOP, EG&G ORTEC model, with 20 % efficiency and 1.9 keV resolution for 1332.49 keV, <sup>60</sup>Co peak. The detector is coupled to an electronic system composed of a multi-channel analyzer, a source of high tension, an amplifier and a compatible microcomputer. The  $\gamma$ -ray spectra were analyzed using the VISPECT 2 software.

### EDXRF and PXRF analysis

Cu, Cr and As were determined in treated massive wood cylinder samples, using a Shimadzu Co. (Kyoto, Japan),

Rany 720 model, EDXRF spectrometer, by the FP (Fundamental Parameters) method. Triplicate measurements were performed and the measurement conditions are shown in Table 2.

The same massive cylinder samples were used for Cu, Cr and As determination by Innov-X System (Woburn, Quebec), Alpha model, PXRF spectrometer, using FP method. Also, triplicate measurements were carried out and the measurement conditions are shown in Table 3.

## Results and discussion

Observed differences between actual (3.9, 6.7, 9.1, 12.4 and 14.0 kg of CCA m<sup>-3</sup> sapwood) and expected retentions (4.0, 6.5, 9.6, 12.8 and 16.0 kg of CCA m<sup>-3</sup> sapwood) showed a 2.5–12.5 % variation, which is in accordance to the literature and is due to natural variability

in wood, mainly in density and different content of cellulose, lignin and moisture [9].

Cu, Cr and As results (mean  $\pm$  SD) plus % RSD values (relative standard deviations) obtained by the related techniques are shown in Table 4. FAAS presented good repeatability, showing a % RSD values  $< 1\%$  (0.1–0.7 %) and INAA presented higher dispersion, 2.1–17.9 % RSD values. EDXRF presented 1.4–8.6 % RSD values and better repeatability was observed for PXRF (0.1–3.1 % RSD values).

Mean values of Cu, Cr and As, determined by FAAS and INAA, were compared using the *t* Student test (Table 5). Mean values for those elements could be considered equal, once the  $t_{crit}$  (6.31)  $>$   $t_{exp}$  values (Cu:  $t_{exp} = 1.57$ –4.04; Cr:  $t_{exp} = 1.47$ –6.24 and As:  $t_{exp} = 2.93$ –6.29). The Center for Forest Resource Technology laboratory at IPT/SP, where the FAAS analysis was carried out, is accredited by INMETRO (Brazilian National Institute of Metrology, Quality and Technology) [21] for AWWPA procedures. This comparison data exercise assured the accuracy of the FAAS method for the determination of those elements in preserved wood.

The EDXRF and PXRF accuracy assessment was performed comparing those results with FAAS data, also applying the *t* Student test (Table 6). Cu and Cr mean values, determined by EDXRF and FAAS, could be considered equal since  $t_{crit}$  (6.31)  $>$   $t_{exp}$  (Cu:  $t_{exp} = 3.42$ –6.25 and Cr:  $t_{exp} = 0.53$ –6.19). Nonetheless, the As values could not be considered equal since  $t_{crit} \ll t_{exp}$ .

The comparison of Cu mean values, obtained by FAAS and PXRF, could not be considered conclusive, once 9.1 and 14.0 mg kg<sup>-1</sup> retentions showed  $t_{crit}$  (6.31)  $>$   $t_{exp}$  (3.59 and 4.35, respectively); however, 3.9, 6.7 and 12.5 mg kg<sup>-1</sup> retentions presented  $t_{crit} <$   $t_{exp}$  values (33.84, 39.18 and 19.45, respectively). Cr and As mean values could not be considered equal since  $t_{exp}$  values showed to be higher than  $t_{crit}$  value ( $t_{exp} \gg t_{crit}$ ), as shown in Table 6.

This study showed that the correction of the absorption effect has to be introduced for As determination in treated wood by EDXRF. Also, the enhancement effect correction has to be introduced for Cr and As determination in preserved wood by PXRF. The introduction of these corrections will be feasible using treated sapwood samples, which were chemically characterized by FAAS and INAA analyses.

## Conclusions

In this study FAAS, INAA and XRF methods were applied for the characterization of treated wood. In EDXRF analysis, AsK $\beta$  fluorescent line suffers absorption effects and in

PXRF CrK $\alpha$  and AsK $\alpha$  fluorescent lines showed enhancement effects. Such effects must be properly corrected for the quantitative determination in treated wood samples using XRF techniques. Three repetitions of the measurements and the application of a *t*-Student test were sufficient for the identification of the absorption and the enhancement effects in Cr and As determination.

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