

Method development of the XRF analysis of metals contents in scots pine wood (*Pinus sylvestris* L.)

TOMASZ ZIELENKIEWICZ

Department of Wood Science and Wood Protection, Faculty of Wood Technology, Warsaw University of Life Science – SGGW

Abstract: *Method development of the XRF analysis of metals contents in scots pine wood (*Pinus sylvestris* L.).* Method of calibration of XRF measurements of metals content in wood was elaborated. Samples of scots pine (*Pinus sylvestris* L.) were examined using XRF spectrometer, then ashed in muffle furnace. Metals content in ash was analysed (XRF) and dissolved. Calibration curves joining results of ashed samples analysis (quantitative) and original samples analysis results (qualitative) were determined. Solutions of ashed samples were also analysed. Additional calibration curves were determined basing on standard solutions of chosen metals nitrates. Calibration curves give possibility of conversion of qualitative results of wood spectrometric analysis to quantitative form (metals content)

Keywords: XRF spectrometer, metal content, scots pine

INTRODUCTION

There are two main sources which can cause raised concentration of metals in wood samples. The air, water and soil pollution in the environment, where tree, which samples are examined, grew up, is one of these sources. Metals compounds can penetrate the tree structure through roots, bark and leaves or conifer needles (Lepp 1975). It is an unfavourable phenomenon in excess: raised concentration of some metals in extreme cases can lead to the atrophy of a tree; besides it can even disqualify wood gained from such a tree as an application material.

Wood preservatives containing metals are the second reason of the increase of metal concentration in wood. Nowadays copper is the most significant metal used in preservatives (e.g. Dr. Wolman 2006). Chromium and arsenic had been also widely applied in preservatives until recently. Metals such as potassium, sodium, mercury were less significant, but used in wood treating. There is much quantity of wooden materials treated with substances containing different metals (sleepers, furniture, building components, works of art etc.).

There is a need to elaborate the fast and precise method of metals analysis in wood because there is a bulk of objects of interest. ICP-MS is the technique which was from years the most often used for metals pollution analysis (e.g. Watmough et al. 1998). Krutul (1996) used another, atomic absorption spectrophotometric (ASA), method for the comparison of the chemical composition of knots and wood of the scots pine (*Pinus sylvestris* L.). Both ICP-MS and ASA techniques require laborious stage of sample preparation. That is why in our paper another technique, X-ray fluorescence (XRF), was applied. The interest in this technique rises nowadays (Rämö et al. 2001; Vives et al. 2005).

In most cases authors confirm the usefulness of XRF technique to metals concentrations analysis and also two of its significant advantages: short stage of sample preparation and non-destructible character of measurements. But its non-destructible character has the negative consequence: elements are examined in some matrix. Modern XRF spectrometers are able to determine elements content in different matrixes: metallic matrix, water matrix, oil matrix, polymer matrix or even wooden matrix. However, each matrix should have its own calibration to give proper, quantitative results. Wooden matrix is the very specific one. Complicated and different for each tree species structure of wood enables the

application of the same calibration to any species. More over, texture of any chosen wood species is heterogeneous (including wood defects), what additionally makes the analysis problematic.

Vives et al. (2005) used thin-film standards to calibrate the system. Rämö et al. (2001) applicated Accu and Merck standards. Results basing on such a calibration, according to the paragraph above, can be quite inaccurate. Mäkinen et al. (2005) stated that empirical calibration of XRF spectrometer is more precise than the fundamental parameter calibration.

The aim of this paper is to elaborate the method of XRF analysis of metal content in wood samples. The method should consist in the calibration process which would eliminate the influence of the specific character of each species matrix on the analysis. This method should also give consideration to the averaging of the metals contents on the specified sample surface, representative in some respect (the surface of annual ring, sapwood, heartwood or the pith, etc.). After the calibration process made for any species, the determining of metals concentrations should be non-destructible and non-time consuming. Application of these kind of calibration eliminates expensive standards purchase.

MATERIALS AND METHODS

Samples of scots pine (*Pinus sylvestris* L.) (one board isolated from sapwood without defects) were the examined material. Six samples with size 5x2,5x1,5 cm were made. Three of them (samples 1, 2, 3) were treated using Wolmanit® CX-10 in order to check the possibility of method application to preserved samples. Vacuum pressure impregnation were carried out in laboratory conditions in the Shel Lab vacuous dryer connected to Büchii vacuous pump. Penetration of pure water into wood sample was examined at first. It was necessary to calculate the preservative concentration, which corresponds to desirable penetration of active substance into wood sample. Samples were treated with Wolmanit® CX-10 solution, concentration corresponding to 4 kg/m³ penetration (IV hazard class). Following parameters were used in applied wood samples treating system: Vacuum pressure in the treating chamber was 0,1 MPa, vacuum time – 20 minutes. After vacuum process system was vented. Sample 1 were taken out from the bath just after venting, sample 2 after 20 and sample 3 after 30 minutes, so the preservative could penetrate samples structure in different degree. In the next step treated wood samples were dried in room temperature during four days. Samples were cut in the centre along fibres and the surface uncovered in this way was analysed using XRF spectrometer.

Residual three samples (4, 5, 6) were analysed unmodified in order to check the possibility of method application to samples with natural (or environmental pollution originated) concentrations of metals, which is much lower than in treated wood. The external sample surface was analysed.

The Spectro Midex M XRF spectrometer was used. “Point scan” option and “mapping” option were used. “Poin scan” examines the chosen point of a sample (2 mm collimator) and gives so called impulse counts (specific for each element) and calculated concentration of different elements. “Mapping” gives the matrix of impulse counts basing on the given surface scanning (point by point, 2 mm collimator) – there are impulse counts given for each element for each point of a scan (map).

Each sample surface was analysed with “mapping” option (map of 24x7 points). Then all samples were ashed (4 hours in the muffle furnace, temperature 600°C). The ash was then pelletized with the pressure of 75 bar. Pellets were analysed using XRF spectrometer. The assumption was made that pellets structure is similar to metallic, homogeneous matrix. Method adapted to metallic matrix was used (results with quantitative character). Ash was then dissolved in the nitric acid solution and neutralized with ammonia. Mixtures was also examined with XRF spectrometer.

Standard solutions of six nitrates were prepared: chromium, copper, iron, zinc, lead, and manganese. Seven solutions for each nitrate were made, corresponding to different metal concentration: 0,5 ppm, 1 ppm, 10 ppm, 50 ppm, 100 ppm, 500 ppm and 1000 ppm (in reality concentration of metals differed from specified above because of ballance accuracy). Standard solutions were also analysed using XRF spectrometer. The dependence between “point scan” results from standard solution measurements and real concentrations was specified. Then results concerning ashed samples solutions could be recalculated. Basing on the results of ashed samples solutions and pelletized ash measurements, mean values of impulse counts (“mapping”) for all examined metals in oryiginal samples were assigned to real concentration. Calibration line could be determined.

It must be emphasize that the calibration process which is quite complicated and time consuming, must be made once for each species. After this process any impulse counts result (from the simple XRF measurement made on the oryiginal wood sample) can be recalculated to real concentration.

RESULTS AND DISCUSSION

Tab. 1 shows real concentration of chosen metals in prepared standard solutions of following salts (pure): $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Tab. 1. Chosen metals concentrations in standard solutions of suitable nitrates.

metal	metal content/ppm						
	solution 1	solution 2	solution 3	solution 4	solution 5	solution 6	solution 7
Cr	0,5	1,0	10,0	50,3	100,0	500,0	1000,0
Cu	0,5	1,0	12,1	50,4	99,5	493,0	999,6
Fe	0,5	1,1	9,9	50,7	99,6	501,3	1000,9
Mn	0,5	1,0	10,1	50,2	98,8	496,9	998,0
Pb	0,5	1,1	10,1	49,4	100,6	499,7	1001,2
Zn	0,5	1,0	10,0	50,6	100,6	499,7	997,0

The dependence of real concentration of chosen metals in standard solutions on the specified with XRF spectrometer average impulse counts is presented in the fig. 1.

Equations of trend lines determined on the fig. 1 and correlation coefficients for all of equations are presented in the tab. 2. Quadratic equation was chosen in respect of higher value of correlation coefficients than for linear equation. The dependence of concentration in ppm (y) on the specific impulse counts (x) is presented. Correlation coefficients for all metals are exceptionally high. It must be emphasize that calculated equations should be applicated only in the range presented above.

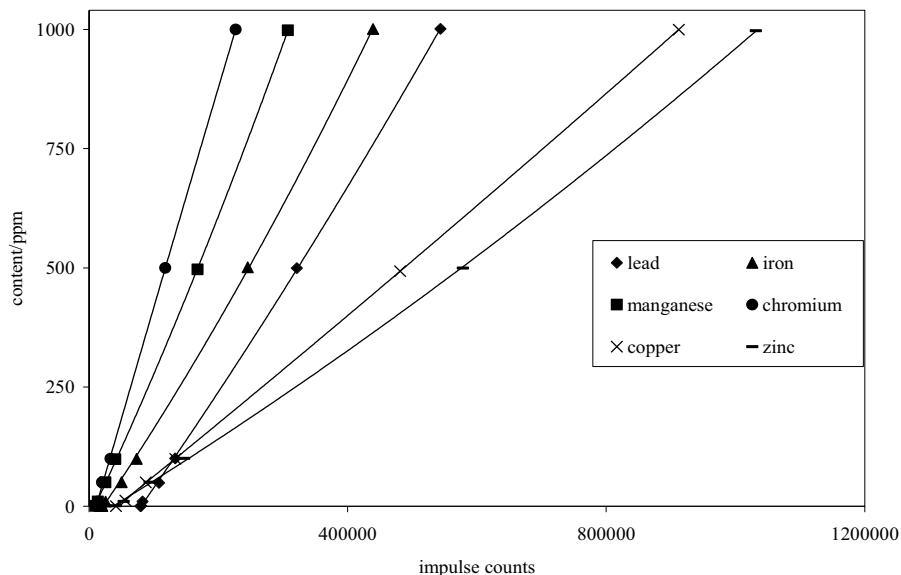


Fig. 1 The dependence of real concentrations of chosen metals in standard solutions on the specified with XRF spectrometer average impulse counts

Tab. 2 Equations of trend lines determined in the fig. 1 and their correlation coefficients

metal	equation	correlation coefficient
Cr	$y = -3 \cdot 10^{-10} x^2 + 0,0047x - 51,23$	0,9999
Cu	$y = 6 \cdot 10^{-11} x^2 + 0,0011x - 46,937$	1
Fe	$y = 9 \cdot 10^{-10} x^2 + 0,002x - 43,23$	0,9998
Mn	$y = 1 \cdot 10^{-9} x^2 + 0,0029x - 25,453$	0,9999
Pb	$y = 5 \cdot 10^{-10} x^2 + 0,0019x - 152,99$	0,9999
Zn	$y = 2 \cdot 10^{-10} x^2 + 0,0008x - 30,834$	0,9999

Tab. 3 contains characteristics of 6 analysed samples before and after ashing and ash dissolving. Data from this table is necessary for further calculations of metals contents.

Tab. 3 Characteristics of examined samples in different analysis stages

sample	sample mass/g	sample mass after ashing/g	mass of dissolved ash/g	mass of ashed sample solution/g
1	7,7323	0,0184	0,0170	34,4541
2	8,0872	0,0270	0,0245	33,8832
3	7,9968	0,0275	0,0261	33,7750
4	9,8333	0,0135	0,0097	47,3221
5	9,8981	0,0153	0,0105	35,9359
6	10,0617	0,0232	0,0189	37,3982

The average impulse counts for ashed samples solutions and calculated metals concentrations are presented in the tab 4a (samples 1-3) and tab 4b (samples 4-6). The third row shows metals concentrations in ashed samples solutions (calculated using equations from the tab. 2). The fourth row contains values of recalculated metals concentrations which concern original wood samples – recalculation basing on masses of solution, ash and original wood sample. Majority of calculated for average impulse counts standard deviations are below 5% of mean value, however in a few cases deviations are still significant.

Tab. 4a Calculated metals concentrations for six metals in ashed samples solutions and in original wood samples (1-3)

metal		Cr	Cu	Fe	Mn	Pb	Zn
average impulse counts in solution	sample 1	6180 ±270	174500 ±2500	19900 ±400	14100 ±1200	81600 ±1900	37400 ±1200
	sample 2	6100 ±400	339000 ±7000	19800 ±600	13100 ±700	82600 ±1400	36300 ±1500
	sample 3	5900 ±210	354000 ±4000	19600 ±600	13000 ±500	80900 ±1500	35400 ±1600
calculated concentration in solution/ppm	sample 1	-*	146,8	-	15,6	5,4	-
	sample 2	-	332,9	-	12,7	7,4	-
	sample 3	-	350,0	-	12,4	4,0	-
calculated concentration in original wood sample/ppm	sample 1	-	708,2	-	75,4	26,0	-
	sample 2	-	1536,9	-	58,7	34,0	-
	sample 3	-	1557,5	-	55,2	17,8	-

*below the equation application range

Tab. 4b Calculated metals concentrations for six metals in ashed samples solutions and in original wood samples (4-6)

metal		Cr	Cu	Fe	Mn	Pb	Zn
average impulse counts in solution	sample 4	6700 ±400	36700 ±1400	21900 ±1300	11800 ±500	82700 ±2400	37800 ±1300
	sample 5	4270 ±290	27000 ±2000	16200 ±800	9700 ±600	80800 ±1400	26900 ±2200
	sample 6	6500 ±400	27900 ±1200	20200 ±500	16000 ±900	83000 ±2000	36300 ±1600
calculated concentration in solution/ppm	sample 4	-*	-	1,0	8,9	7,6	-
	sample 5	-	-	-	2,8	3,8	-
	sample 6	-	-	-	21,2	8,2	-
calculated concentration in original wood sample/ppm	sample 4	-	-	6,7	59,6	50,6	-
	sample 5	-	-	-	14,7	20,1	-
	sample 6	-	-	-	96,7	37,2	-

*below the equation application range

Calculations of metals concentrations in original samples basing on pellets analysis is presented in the tab. 5. Concentration in original wood samples is calculated basing on the

content of ash in wood samples. Values of standard deviations for average concentration in pellets are much higher than for ash solutions. It is because after dissolution sample is homogenized.

Tab. 5 The relation between metals concentrations in pellets and original wood samples

metal		Cr	Cu	Fe	Mn	Pb	Zn
average metals concentrations in pellets/%	sample 1	-*	11,4 ±2,5	0,089 ±0,026	1,42 ±0,06	-	0,078 ±0,009
	sample 2	-	21,5 ±0,7	0,054 ±0,022	1,19 ±0,11	-	0,0332 ±0,0024
	sample 3	-	22,3 ±1,1	0,032 ±0,015	1,18 ±0,07	-	0,014 ±0,007
	sample 4	-	0,024 ±0,003	0,031 ±0,011	1,46 ±0,13	0,03 ±0,014	0,0416 ±0,0023
	sample 5	-	0,022 ±0,004	0,032 ±0,012	1,31 ±0,04	-	0,0372 ±0,0025
	sample 6	-	0,016 ±0,007	-	1,49 ±0,05	-	0,0475 ±0,0020
calculated concentrations in wood samples/ppm	sample 1	-	271,3	2,11	33,8	-	1,86
	sample 2	-	717,8	1,80	39,7	-	1,11
	sample 3	-	766,9	1,10	40,6	-	0,48
	sample 4	-	0,33	0,43	20,0	0,41	0,57
	sample 5	-	0,34	0,49	20,2	-	0,58
	sample 6	-	0,37	-	34,4	-	1,10

* below detection limit

Tab. 6 includes final equations for each metal which connect the average impulse counts ("mapping") from original samples with real concentrations basing on ashed samples solutions (column 2) and pellets (column 4) analysis. Mean impulse counts in original wood samples is x value, concentration in ppm corresponds to y value.

Tab. 6 Final calibration curves equations basing on ashed samples solutions (column 2) and pellets (column 4) analysis

metal	calibration curve equation (solutions)	correlation coefficient	calibration curve equation (pellets)	correlation coefficient
Cr	-	-	-	-
Cu	$y=0,0203x-1166$	0,9514	$y=1,172*10^{-14}x^{3,283}$	0,9995
Fe	-	-	$y=0,00209x-14,237$	0,9599
Mn	$y=0,0677x-414,62$	0,8832	$y=0,0114x-54,771$	0,9449
Pb	$y=0,5806e^{0,0002x}$	0,9243	-	-
Zn	-	-	$y=0,000269x-3,7635$	0,8646

It must be emphasized that presented equations can be applied in the range of extreme analysed values (presented in tables 4 and 5), possibly close extrapolation is allowed.

Correlation coefficients of presented equations are acceptable. Some of measuring points (maximum 2 for one metal) were acknowledged as blunders and excluded from calculations. In case of zinc and manganese (pellets analysis) these points correspond to sample 2 and 3, which contain very high amount of copper, introduced during wood

treatment. High content of copper seem to disturb other metals analysis. Locally rised copper concentration in pellets can falsify results for other metals.

Dependences for manganese and copper obtained with two methods differ significantly. Differences are probably caused by high standard deviations of mean values (especially in pellets analysis) and different ranges of analysis (in case of copper).

The dependence for chromium was not found at all. It is because of relatively low content of this metal in wood. It is possible to obtain calibration curve for low concentrations basing on ashed samples solutions, but these solutions must be condensed.

CONCLUSIONS

1. The method is promising but it needs optimization.
2. Ashed samples (especially treated ones) should be homogenized before analysis, using, for example, agate mortar.
3. Ash should be dissolved in as low amount of solvent as possible (in boiling point under a reflux condenser) in order to raise metals concentration in solutions.
4. Different calibration curves should be applicated to significantly different concentration ranges of metals in wood (e.g. native and wood treating originated content of copper).
5. Significantly higher samples amount should be used for calibration process.
6. Results should be verified using another method of instrumental analysis. Process of ashing may cause the decrease of some metals content (volatile compounds).

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Steszczenie: *Opracowanie metody analizy XRF zawartości metali w drewnie sosny zwyczajnej (Pinus sylvestris L.).* Opracowano metodę kalibracji pomiarów XRF na drewnie sosny zwyczajnej. W tym celu próbki sosny zostały przeanalizowane na spektrometrze (wyniki o charakterze jakościowym), a następnie spopielone w piecu muflowym. Uzyskany popiół został przebadany przy użyciu tego samego spektrometru na zawartość metali (wyniki o charakterze ilościowym). Wyznaczono krzywe kalibracyjne łączące wyniki analizy (zawartości metali) popiołu i próbek wyjściowych. Spopielone próbki zostały rozpuszczone, a roztwory tak samo przebadane. Wyznaczono dodatkowe krzywe kalibracyjne będące zależnością między wynikami analizy roztworów spopielonych próbek i próbek wyjściowych. Efektem pracy jest możliwość konwersji wyników spektrometrycznej analizy drewna (o charakterze jakościowym) do formy o charakterze ilościowym (zawartość metali) przy użyciu wyznaczonych krzywych kalibracyjnych.

Corresponding author:

Tomasz Zielenkiewicz
Department of Wood Sciences and Wood Protection,
Faculty of Wood Technology,
Warsaw University of Life Sciences – SGGW,
Ul. Nowoursynowska 159,
02-776 Warsaw,
Poland
e-mail: tomasz_zielenkiewicz@sggw.pl