

## Investigations of iron content in fossil oak from a medieval settlement in Płońsk

PIOTR MAŃKOWSKI, PAWEŁ KOZAKIEWICZ, TOMASZ ZIELENKIEWICZ  
Warsaw University of Life Science – SGGW, Department of Wood Science and Wood Protection

**Abstract:** *Investigations of iron content in fossil oak from a medieval settlement in Płońsk.* A slice of fossil oak obtained from an excavation site in Płońsk was dried, its surface was prepared accordingly, and then it was subjected to XRF analysis. The test determined the iron content along a specified test line on the cross section of a former structural element. For the sake of comparison, analogous tests were carried out for contemporary oak wood. The results show a nonuniform distribution of iron on the surface of the fossil oak sample obtained from the excavations. The part of sapwood and pith had lower iron content, similarly as the heartwood in the geometric centre of the former structural element; while high iron content was observed in the heartwood along its limit.

*Keywords:* excavations, archeological wood, Płońsk, oak wood, iron, XRF

### INTRODUCTION

Oak, as one of the naturally most durable kinds of domestic wood, is characterised by high resistance to biotic factors and can remain for many years lying in layers of wet soil, thanks to which it is a common element of archaeological findings (e.g. Krutul and Kozakiewicz 1999 and 2003, Kozakiewicz 2008, Krutul et al. 2010, Jankowska and Kozakiewicz 2011).

After prolonged contact with iron compounds in moist environment, oak wood gradually changes its natural colour to greyish-black. In that form, it is known as fossil oak or black oak. The black colour is related with the increased content of iron compounds (e.g. Krzysik 1978, Krutul and Kozakiewicz 1999 and 2003, Krutul et al. 2010).

This raw material has always been eagerly used to manufacture, among other things, decorative floors and furniture, as well as other wooden objects. Nowadays, fossil oak is often used in renovation and reconstruction of antique objects, in order to preserve the authenticity of materials.

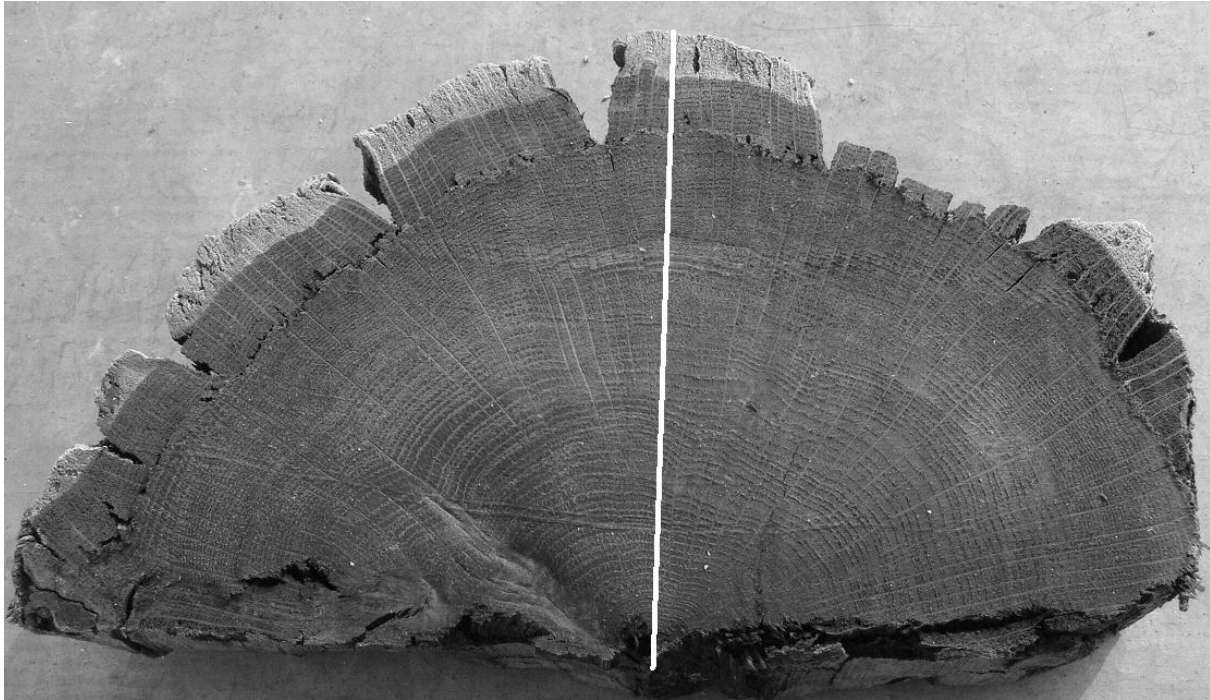
XRF spectroscopy is being successfully used to test wood. This method has served to determine, among other things, the content of: copper (Zawadzki et al. 2010), chlorine (Zielenkiewicz et al. 2009) or lead (de Vives et al. 2007), as well as the efficiency of iron(III) salt penetration into oak wood (Mańkowski et al. 2010).

### MATERIAL AND METHODS

The oak wood used in the investigations was obtained from an archaeological site in a medieval settlement outside the city walls of Płońsk, near river Płonka and close to the Kabana hill. The excavations were performed due to the construction of the Płońsk bypass. The age of the wood was estimated on the basis of pottery fragments found close by (the ornaments visible on pottery fragments was characteristic for the 11th century).

A typical structural element used in construction, 2.2m long and made of a half tree-trunk, was chosen for the investigations. The wood was obtained wet (Kozakiewicz, Mańkowski 2012). The dominant heartwood was saturated with iron compounds and had an intense dark colour (blackish-grey), while the lighter, narrow zone of sapwood was decayed by microorganisms to a large degree (Fig.1).

A slice of wood, about 2 cm thick, was cut from the above-mentioned structural element at the distance of ca. 1 m from its front; and afterwards it underwent a slow drying process. After drying, the surface was flattened and tested with an X-ray fluorescence spectrometer – Spectro Midex M. The tests were made on a test line that ran along a radius of the cross section, from the pith to the circumference of the original tree-trunk (Fig.1). We determined the iron content; each testing point with the diameter of 0.6 mm was tested during 30 sec. Additionally, the moisture, growth ring width and wood density were also tested in accordance with Polish standards (PN-D-04110:1955, PN-D-04100:1977 and PN-D-04101:1977). A contemporary oak samples with similar dimensions, width and growth ring layout was used as a reference material. The same measurement methods were applied.



**Fig.1.** Slice of fossil oak with the testing line marked (in white) for XRF spectrophotometer tests

## RESULTS AND DISCUSSION

In the tested slice of fossil oak, heartwood had 92 annual rings, while sapwood had 14 rings. The element had diameter of ca. 220 mm. There were 106 growth rings on a radius section of 105 mm (it is wood of slow growth with average growth ring width of ca. 1 mm). The density of archaeological wood's heartwood in air-dry state amounted to  $860 \text{ kg/m}^3$  on average, while in case of the highly degraded (probably by anaerobic bacteria) sapwood, it was only  $340 \text{ kg/m}^3$ .

The fossil oak wood under investigation was characterised by a nonuniform distribution of iron. The highest concentration was observed next to the edge of the structural element (an evident increase of content from the side of the pith and in the heartwood closer to the tree-trunk edge – on the limit with sapwood).

The iron content measured with the XRF spectrophotometer decreased gradually towards the geometrical centre of the cross section of the fossil oak slice obtained from the excavations. That decrease in the zone of heartwood is represented by a 2nd order polynomial curve (Fig.2.) with a high coefficient of determination ( $r^2=0.81$ ). The original pith of the excavated oak and its sapwood part contained much less iron (the results of iron measurements were comparable with the area of heartwood in the centre of the element's section). The distribution of iron on the cross section of the contemporary samples was

uniform (along the measurement line along the radius), and the content of iron was much lower in comparison with fossil oak. Moreover, we observed a slight increase of iron content in the bark of contemporary oak wood.

The above-mentioned test results confirm previous observations of iron distribution in fossil oak, among others on the cross section of a 160 year old bridge pole that served as a support for a stone bridge on river Limmat in Zürich, Switzerland (Krutul et al. 1998). The processes of iron penetration and its bonding by the tannins present in oak wood that lied in moist environment, are most intense in the element layers that are close to the surface (the layers closer to the middle are naturally isolated). As a result, a nonuniform iron content distribution can be observed. The sapwood and the pith parenchyma of oak, due to the naturally lower tannin content, do not have the property of intense bonding with iron compounds that heartwood has.

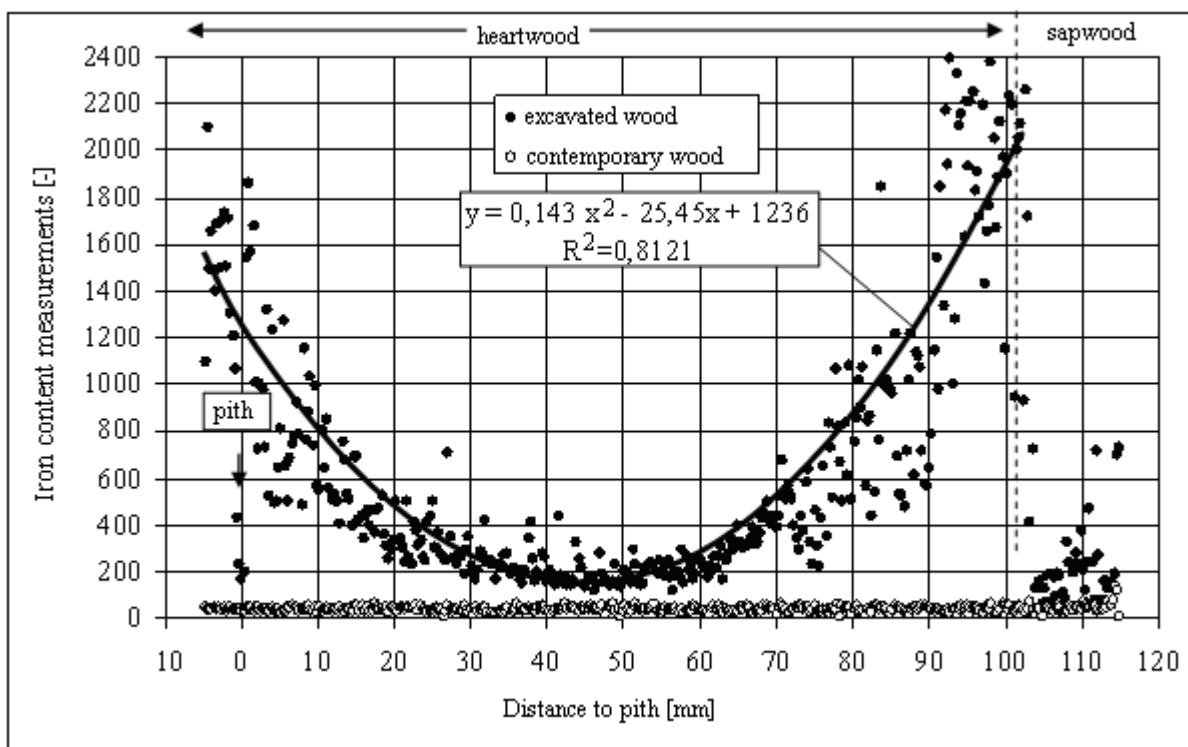


Fig.2. Results of iron content measurements in contemporary and excavated oak wood

## CONCLUSION

On the basis of the performed tests, the following conclusions have been drawn:

1. The slow growth wood of fossil oak obtained from excavations was characterised by a nonuniform state of preservation determined on the basis of air-dry density. While the heartwood was very well preserved, the sapwood's density was 2.5 times lower.
2. In comparison with contemporary oak wood, the content of iron was visibly higher on the entire cross section of the medieval structural element from Płońsk that was preserved in moist environment as fossil oak.
3. The distribution of iron in the excavated wood was not uniform. The highest iron concentration was observed in the area of heartwood next to the external edge of the former structural element. A significantly lower iron content on the cross section was observed in the areas of pith, sapwood and in the heartwood area closer to the centre of the element.

## REFERENCES

1. DE VIVES A. E. S., MOREIRA S., BRIENZA S. M. B., MEDEIROS J. G. S., FILHO M. T., ARAUJO O. L., ZUCCHI D., DO NASCIMENTO FILHO V. F., BARROSO R. C., 2007: Species arboreal as a bioindicator of the environmental pollution: Analysis by SR-TXRF. *Nuclear Instruments and Methods in Physics Research A*, 579, 494–498.
2. JANKOWSKA A., KOZAKIEWICZ P., 2011: Identification research on charcoals and the imprint on concrete element from an Novae archeological excavation site in north Bulgaria. *Annals of Warsaw University of Life Sciences – SGGW, Forestry and Wood Technology* No 74, s.115-119.
3. KOZAKIEWICZ P., 2008: Makroskopowe rozpoznanie rodzajów drewna z obiektów pozyskanych w trakcie badań archeologicznych na terenie średniowiecznego miasta w Pucku, ekspertyza.
4. KOZAKIEWICZ P., MAŃKOWSKI P., 2012: Rozpoznawanie rodzajów drewna z obiektów pozyskanych w trakcie badań archeologicznych na terenie średniowiecznego podgrodzia w Płońsku, ekspertyza.
5. KRUTUL D., KOZAKIEWICZ P., 1999: Zawartość substancji mineralnych w drewnie dębowym po wieloletnim oddziaływaniu środowiska wodnego. *Folia Forestalia Polonica Seria B Drzewnictwo, zeszyt 30, 1999, str.: 95-102.*
6. KRUTUL D., KOZAKIEWICZ P., 2003: Impact of chemical factors on concentration changes of selected elements in native oak wood and excavated oak wood. *Annals of Warsaw Agricultural University. Forestry and Wood Technology* No 53, s.199-202.
7. KRUTUL D., KOZAKIEWICZ P., BERNATOWICZ G., NIEMZ P. 1998: Wpływ wieloletniego oddziaływania środowiska wodnego na skład chemiczny drewna dębowego. *Materiały 12 Konferencji Naukowej Wydziału Technologii Drewna SGGW „Innowacyjność badań w przemyśle i nauce”. Warszawa, 17-18 listopada 1998r. str.:191-199.*
8. KRUTUL D., RADOMSKI A., ZAWADZKI J., ZIELENKIEWICZ T., ANTCZAK A., 2010: Comparison of the chemical composition of the fossil and recent oak wood. *Wood Research* 55(3): 2010 113-120.
9. KRZYSIK F., 1978: *Nauka o drewnie*. PWN. Warszawa.
10. MAŃKOWSKI P., ZIELENKIEWICZ T., BORUSZEWSKI P., 2010: Iron chloride solution penetration into oak wood. *Annals of Warsaw Agricultural University. Forestry and Wood Technology*, 71, 490-494.
11. PN-55/D-04110 Fizyczne i mechaniczne własności drewna. Badanie procentowego udziału drewna wczesnego i późnego
12. PN-D-04100:1977 Drewno. Oznaczanie wilgotności.
13. PN-D-04101:1977 Drewno. Oznaczanie gęstości.
14. ZAWADZKI J., ZIELENKIEWICZ T., RADOMSKI A., WITOMSKI P., DROŻDŻEK M., 2010: Testing content of copper in Scots pine wood (*Pinus sylvestris* L.) after preservative treatment. *Wood Research*, 55, 4, 91-100.
15. ZIELENKIEWICZ T., RADOMSKI A., ZAWADZKI J., NIESŁOCHOWSKI A. 2009: Migrations of chlorine compounds in pine wood samples (*Pinus sylvestris* L.). *Annals of WULS SGGW, For. and Wood Technol.*, 69, 480-484.

**Streszczenie:** *Badania zawartości żelaza w drewnie czarnej dębiny ze średniowiecznego podgrodzia w Płońsku.* Próbkę pozyskaną z całego przekroju poprzecznego odnalezionego elementu konstrukcyjnego (ociosana polówka pnia dębowego o średnicy ok. 200 mm) podczas prac wykopaliskowych w Płońsku, po wysuszeniu i przygotowaniu powierzchni poddano analizie XRF. Określano zawartość żelaza na linii pomiarowej biegnącej promieniowo na przekroju poprzecznym od rdzenia do pobocznic pierwotnego pnia (dawnego elementu konstrukcyjnego). Dla porównania przeprowadzono analogiczne badania dla drewna dębu współczesnego. Stwierdzono nierównomierny rozkład żelaza na powierzchni próbki czarnej dębiny. Największe stężenie żelaza występowało w twardzieli dębowej przy obrysie dawnego elementu konstrukcyjnego charakteryzującego się najsilniejszą zmianą barwy (bliską czarnej), natomiast w jego części centralnej oraz w okolicy rdzenia i bielu stężenie żelaza było zdecydowanie niższe. Rozkład żelaza na przekroju poprzecznym współczesnego drewna dębowego był równomierny, a jego ilość zdecydowanie mniejsza niż w czarnej dębinie z średniowiecznego podgrodzia w Płońsku.

Corresponding author:

Ph.D. Piotr Mańkowski  
Department of Wood Science and Wood Protection  
Warsaw University of Life Science – SGGW  
02-776 Warszawa, Nowoursynowska 166  
Poland  
e-mail: piotr\_mankowski@sggw.pl  
tel. +48 22 59 386 38