TREE-RING RESEARCH, *Vol. 61(2), 2005, pp. 87–92*

RESEARCH REPORT

LASER TRIMMING TREE-RING CORES FOR DENDROCHEMISTRY OF METALS

PAUL R. SHEPPARD*

Laboratory of Tree-Ring Research
University of Arizona, Tucson, Arizona 85721, USA

and

MARK L. WITTEN

Department of Pediatrics
University of Arizona, Tucson, Arizona 85721, USA

ABSTRACT

This article discusses the application of laser to trim the outer surface from tree-ring increment cores in preparation for dendrochemistry of certain metals. A source of contamination specific to dendrochemistry of metals is metal constituents, such as iron, tungsten, chromium, nickel, and cobalt, coming off tools used to collect and process cores and adhering to the sample surface. One method to eliminate this contamination is to trim off the outer surface of cores using laser. To test this application of laser, three tree-ring increment cores were collected from each of three trees. For each tree, one core was trimmed using a CO_2 laser, one core was trimmed using a stainless steel razor blade, and one core was left untrimmed. The resultant cores were measured for metals using acid dissolution inductively coupled plasma mass spectroscopy. Trimmed cores had on average one-third the content of iron, tungsten, and chromium than that of untrimmed cores. Laser-trimmed cores had less of these metals than razor-trimmed cores. Razor-trimmed cores also had measurable nickel, but laser-trimmed cores had no nickel. Laser trimming is an ideal solution to potential contamination of cores with metals from increment borers without imparting other contamination from tools such as razor blades.

Keywords: dendrochemistry, tree rings, metals, contamination, laser.

INTRODUCTION

This article discusses the application of laser to trim the outer surface from tree-ring increment cores in preparation for dendrochemistry of certain metals. Dendrochemistry, the analysis and interpretation of chemical elements in tree rings (Amato 1988; Lewis 1995), has special sample preparation requirements to avoid contaminating specimens with elements of research interest (Smith and Shortle 1996). For example, contamination might occur from dropping specimens on the ground, from not fully cleaning tree-ring borers from one tree to the next and thereby intermixing sap across different trees, or from using contaminated reagents in chemical procedures of sample digestion.

An additional contamination specific to dendrochemistry of metals is metal constituents coming off tools used to collect and process cores and adhering to sample surfaces. This contamination stems from the Locard Exchange Principle, which asserts that whenever two objects touch one another, some amount of transfer of their material takes place between them (Murray and Tedrow 1992). For example, stainless steel is composed of iron (the ''steel'') with anywhere from 11 to 30%

*Corresponding author: sheppard@ltrr.arizona.edu

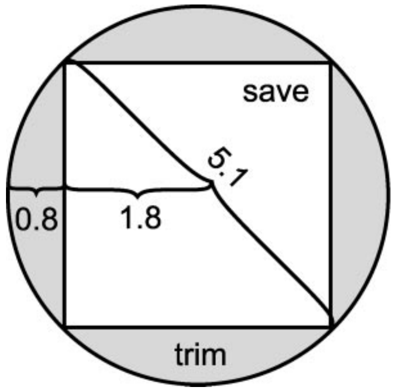

Figure 1. End view of a tree-ring core. Lengths are in mm. Shaded areas are surface segments to be trimmed, and the white area is the inner-core to be saved.

chromium added to avoid rusting (the ''stainless'' part) plus minor amounts of nickel (Lula 1986). Using stainless steel tools on tree-ring specimens for dendrochemical investigations of these metals poses contamination questions because some amount of these metals could transfer from the tools to the wood.

For collecting increment cores in the field, steel (iron) increment borers used widely in dendrochronology (Phipps 1985) are also commonly used in dendrochemistry. Increment borers can be stainless steel, or they can be reinforced with other metals. For example, tungsten can be added to steel to increase its strength throughout the entire tool by ''dispersion hardening'' (Harris and Humphreys 1983); increment borers made of steel reinforced in this manner should contain tungsten throughout the entire shaft. Consequently, in dendrochemistry of iron and tungsten, there is an inherent risk of sample contamination from the borer itself. This contamination should be eliminated prior to measuring tree-ring samples for determining temporal changes in environmental availability of these metals.

Given that contamination from increment borers should be limited primarily to the surface of cores, a reasonable way to eliminate it would be to trim off the outer surface, leaving an inner-core untouched by the borer (Figure 1). Multiple options exist for trimming the surface from cores. Regular sanding could remove the surface, but sanding should be avoided in dendrochemical studies because it spreads dust of all rings across all parts of the sanded core (Pearson *et al.* 2005). Trimming with razor blades would also work, but razors could potentially contaminate the inner-core of samples with their own constituents, for example with iron, chromium, and nickel in the case of stainless steel blades.

Another option is laser, which has long been used in various medical and biological applications to cut many types of materials (Martyr 1984; Vij and Mahesh 2002). Indeed, laser has been used to cut wood up to a couple cm in thickness (Peters and Marshall 1975), and modern laser systems are powerful enough to cut through wood several cm in thickness. If laser could be applied to trim the surface from tree cores, then the resultant inner-cores would theoretically be free of contamination from metal tools of dendrochemistry. The objective of this research was to test this application of laser and to quantify its performance for the metals contained in increment borers and razor blades, namely iron, tungsten, chromium, and nickel.

METHODS

Tree-Ring Samples

Tree-ring increment cores were collected from three tree species. To represent gymnosperms, Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) and ponderosa pine (*Pinus ponderosa* Dougl. ex. Laws.) were selected because they are prominent species in dendrochronology generally (Grissino-Mayer 1993) and because they are favorable species for dendrochemistry specifically (Cutter and Guyette 1993). To represent angiosperms, cottonwood (*Populus* spp. L.) was chosen because it is commonly planted for landscaping and therefore might be readily available for dendrochemistry in urban areas.

For each species, cores were collected from one tree growing near Tucson, Arizona (32°11′N, 110°52′W). The Douglas-fir and ponderosa pine were growing in natural forests and the cottonwood was growing in a natural desert wash; none of the sampling sites was near any point source for metals pollution. From each tree, three 10-cm-long cores were collected from the same radial direction and just a few cm from one another up and down

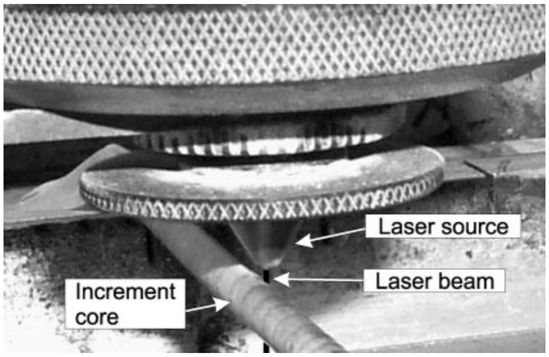

Figure 2. Laser trimmer in use, trimming an increment core without touching it.

the tree. With this strategy, the three cores within each tree were as similar to each other as possible. The cores were collected using a Haglof 5.1-mm-diameter increment borer and then allowed to air dry. The cores were not glued into protective mounts, but rather they were merely tied to mounts using thread.

Sample Preparation

For each tree, one core was trimmed using laser (Figure 2). Laser trimming was done with a 1-Watt CO_2 laser focused into a cutting beam 0.038 mm in diameter. The cores were held in place with an aluminum grip that was attached to a part of the cores that was not to be measured. Air was injected during trimming to flush away cutting debris. Combustion of the wood samples was avoided by cutting quickly, but mild charring remained on the surface of the inner-cores.

One of the other cores was trimmed using a new Personna brand stainless steel razor blade (American Safety Razor Company, Verona, Virginia). The remaining core was left untrimmed to serve as a control comparison for the two trimmed cores. After trimming, all cores were divided radially into thirds using a non-metallic, ceramic knife. This provided separate temporal sections of the innermost (closest to pith), middle, and outermost (closest to bark) rings of the samples.

Chemical Measurement of Metals

For trace metal measurements, the cores were prepared via acid digestion followed by analysis with a high-resolution inductively coupled plasma mass spectrometer (ICP-MS). Wood samples were weighed into precleaned, pre-weighed, trace metal-free polypropylene centrifuge tubes. For every 25 mg of sample, 1 mL of concentrated Optima grade nitric acid (HNO_3) was added to the tube. The samples were allowed to sit at room temperature for two days and then were digested at 70°C in an ultrasonic bath for 3 hours. After digestion was complete, the sample tubes were reweighed in order to calculate dilution factors. After thorough mixing, an aliquot of the digestate (approx. 0.25 g) was gravimetrically diluted by a factor of approximately 20 with ultrapure 18.2-megaOhm/cm water. Internal standards of scandium and indium were also added.

To calibrate the VG Axiom High-Resolution ICP-MS, linearity standards were prepared. These standards were diluted from multi-element calibration standards obtained from High Purity Standards. Scandium and indium were added to the linearity standards at approximately 20 ppb for scandium and 10 ppb for indium. Five standard points were used to calibrate the instrument for all elements of interest. The concentrations for all standards were used to create the linear calibration curve of instrument response versus concentration for each analyte.

The following elements were measured: lithium, beryllium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and strontium, arsenic, molybdenum, silver, cadmium, tin, antimony, cesium, tantalum, tungsten, thallium, lead, thorium, and uranium. Limits of detection were all $\leq$200 ppb, with many elements having a limit of detection $\leq$10 ppb.

Data Analysis

Iron, tungsten, cobalt, chromium, and nickel were the metals of highest interest in this research, and they were evaluated quantitatively and qualitatively for the effect of trimming treatments within tree species. To test for statistical significance of metal concentrations, various one-way analyses of variance (ANOVA, Sokal and Rohlf 1981) were performed with trimming method, temporal segment, and tree species used as single, separate treatment factors with all other factors being pooled together to maximize the error degrees of freedom. For metals that showed similar patterns of contamination but with different absolute concentrations, values were normalized within each metal in order to allow pooling across metals for yet more error degrees of freedom.

RESULTS

Most of the elements measured in this study did not show any particular patterns that would indicate contamination from either the increment borer or the razor blade. In contrast to this lack of pattern, iron, tungsten, and chromium showed a consistent pattern of contamination across the trimming treatments for all three tree species (Figure 3). Trimmed cores had on average one-third the content of these metals than untrimmed control cores. Additionally, laser-trimmed cores typically had less of these metals than razor-trimmed cores. The ANOVA of normalized data from all three metals with trimming as the main factor was very significant ($F = 66.5$, $df = 2$ and 75, $p < 0.001$). The ANOVAs with treatment factors of tree species ($F = 1.3$, $df = 2$ and 75, $p = 0.28$) and temporal segment ($F = 1.6$, $df = 2$ and 75, $p = 0.20$) were not significant.

Untrimmed cores also showed high temporal variability in iron, tungsten, and cobalt, whereas laser-trimmed cores showed little variability. Again using normalized values within each metal, Levene's test of equality of variances (Sokal and Rohlf 1981) across all three metals with trimming as the main factor was very significant ($p < 0.001$). Unequal variance in this case might appear to invalidate ANOVA testing because one of the assumptions of ANOVA is equal variance across treatments (Sokal and Rohlf 1981). However, ANOVA is robust to moderate violations of this assumption (Jackson and Brashers 1994). Furthermore, unequal variance can be interpreted as yet more evidence of a strong treatment effect (Anderson 2001).

Nickel showed a different pattern of contamination across trimming treatments, again consistently for all three tree species (Figure 3). Razor-trimmed cores had measurable nickel, but most untrimmed and all laser-trimmed cores had less than the detection limit. The ANOVA of nickel data with trimming as the main factor was very significant ($F = 17.2$, $df = 2$ and 23, $p < 0.001$). The ANOVAs with treatment factors of tree species ($F = 0.7$, $df = 2$ and 23, $p = 0.52$) and temporal segment ($F = 0.4$, $df = 2$ and 23, $p = 0.69$) were not significant.

The effect of contamination from metal tools was not consistent through the temporal sequence of the cores (Figure 3). From the increment borer, outermost rings of the Douglas-fir and the cottonwood had the highest amounts of iron, tungsten, and chromium whereas innermost rings of the ponderosa pine had the highest amounts of these metals. From the razor blade, middle rings of the ponderosa pine and the cottonwood had the highest amount of nickel whereas outermost rings of the Douglas-fir had the highest amount of this metal. The statistical significance of these temporal patterns cannot be determined because of lack of replication within each tree species.

DISCUSSION

Increment borers, the predominant field tool for collecting dendrochronological samples, can lose some of their primary constituent metals of iron and tungsten onto cores. Borers can also leave traces of chromium on cores. The magnitude of this contamination can be large relative to the trace amounts of these metals that might exist in cores, and adding such a large contamination to the true contents would damp environmental variability that might exist through time, perhaps to the point of making it difficult to discern meaningful environmental signals. Furthermore, contamination from borers is not consistent across different temporal segments of cores, indicating that neither the Locard exchange of metals nor the potential translocation of metals by internal wood moisture of living trees is constant across rings of a core.

Preparation of cores for dendrochemistry of these metals should include removing this contamination by the increment borer. Laser is very effective at removing this contamination from cores by trimming their surfaces. Laser can trim off the surface without unduly damaging the inner-core.

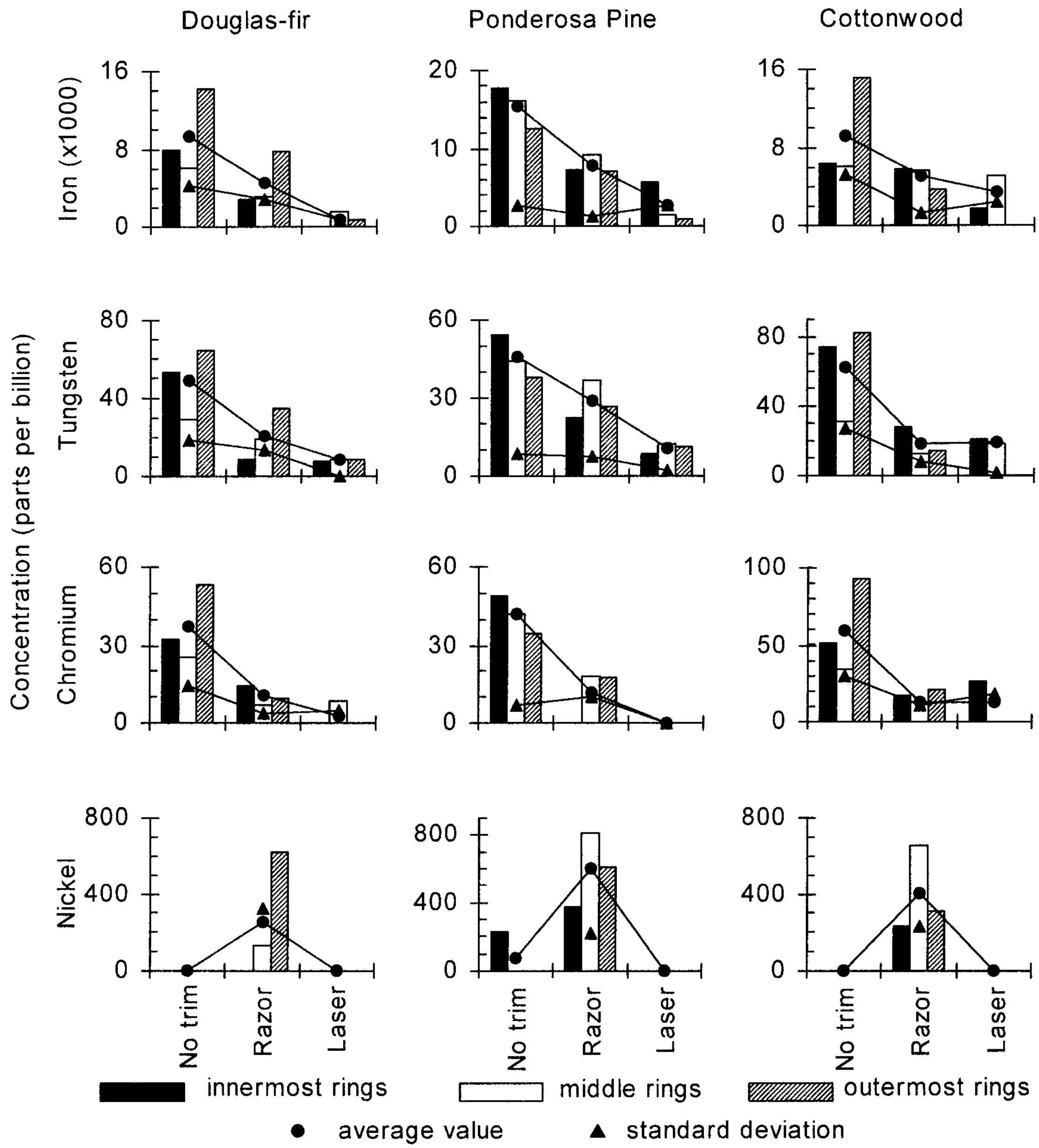

Figure 3. ICP-MS results for each core of each tree species for tungsten, chromium, iron, and nickel. Solid bars represent innermost rings, open bars represent middle rings, and hatched bars represent outermost rings. Within trimming treatments, filled circles are average contents and filled triangles are standard deviations. Values for the laser-trimmed, cottonwood, outermost-rings sample are missing because that sample was lost, but all other apparently missing bars represent values of less than the limit of detection.

Charring on the surface of the inner core caused by the laser can make it difficult to see growth rings clearly, so prior to laser trimming, the ring boundaries should be identified and marked on the core mount for later reference. The resultant inner-core is untouched by metal tools, and in the cases of the three trees tested here, low temporal variability of the metals after laser trimming confirms the expectation of little to no change in the environmental availability of these metals over the last several years. Laser trimming appears to be an ideal solution to potential metals contamination of cores from increment borers and other tools.

Razor trimming of cores is somewhat effective at removing contamination of iron, tungsten, and chromium from increment borers. However, temporal variability of these metals is higher with razor trimming than with laser trimming, and stainless steel razor blades can impart their own contamination onto cores, for example, nickel from the blade used in this research. If nickel were part of a dendrochemistry research objective, then razor trimming would not be acceptable.

CONCLUSIONS

For dendrochemistry of metals contained in increment borers and other laboratory tools, contamination is likely to occur while collecting cores and preparing samples for measurement. This contamination is limited to the outer surface of the cores, which can be removed through trimming. Among various options for trimming, laser works well because it removes the surface without using metal tools.

ACKNOWLEDGMENTS

Gary Huckleberry, Jeff Dean, Jeff Speakman, Carl Welch, and Mark Borgstrom assisted in this project. Chemical measurements were made by the Analytical Chemistry Group at the University of Missouri Research Reactor Center. This research was funded in part by the Gerber Foundation and the Cancer Research and Prevention Foundation.

REFERENCES CITED

Amato, I.
1988 Tapping tree rings for the environmental tales they tell. *Analytical Chemistry* 60(19):1103A–1107A.

Anderson, N. H.
2001 *Empirical Direction in Design and Analysis.* Lawrence Erlbaum Associates, Mahwah, New Jersey; 862 pp.

Cutter, B. E., and R. P. Guyette
1993 Anatomical, chemical, and ecological factors affecting tree species choice in dendrochemistry studies. *Journal of Environmental Quality* 22(3):611–619.

Grissino-Mayer, H. D.
1993 An updated list of species used in tree-ring research. *Tree-Ring Bulletin* 53:17–43.

Harris, P. M., and D. S. C. Humphreys
1983 *Tungsten: A Review.* Occasional Papers of the Institution of Mining and Metallurgy, Paper 2. Institution of Mining and Metallurgy, London.

Jackson, S., and D. E. Brashers
1994 *Random Factors in ANOVA.* Sage Publications, Thousand Oaks, California; 66 pp.

Lewis, T. E. (ed.)
1995 *Tree Rings as Indicators of Ecosystem Health.* CRC Press, Boca Raton, Florida; 210 pp.

Lula, R. A.
1986 *Stainless Steel.* American Society for Metals, Metals Park, Ohio; 173 pp.

Martyr, D. R.
1984 Laser cutting—a new tool for shipbuilding. In *Laser Welding, Cutting, and Surface Treatment,* edited by R. Crafer, pp. 28–32. The Welding Institute, Cambridge, England.

Murray, R. C., and J. C. F. Tedrow
1992 *Forensic Geology.* Prentice Hall, Englewood Cliffs, New Jersey; 203 pp.

Pearson, C., S. W. Manning, M. Coleman, and K. Jarvis
2005 Can tree-ring chemistry reveal absolute dates for past volcanic eruptions? *Journal of Archaeological Science* 32:1265–1274.

Peters, C. C., and H. L. Marshall
1975 Cutting wood materials by laser. *USDA Forest Service Research Paper* FPL-250. 10 pp.

Phipps, R. L.
1985 Collecting, preparing, crossdating, and measuring tree increment cores. *US Geological Survey Water Resources Investigations* Report 85-4148. 48 pp.

Smith, K. T., and W. C. Shortle
1996 Tree biology and dendrochemistry. In *Tree Rings, Environment, and Humanity,* edited by J. S. Dean, D. M. Meko, and T. W. Swetnam, pp. 629–635. Radiocarbon, Tucson, Arizona.

Sokal, R. R., and F. J. Rohlf
1981 *Biometry.* W. H. Freeman and Company, San Francisco; 219 pp.

Vij, D. R., and K. Mahesh (eds.)
2002 *Medical Applications of Lasers.* Kluwer Academic Publishers, Boston; 375 pp.

Received 9 September 2005; accepted 14 November 2005