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Technical note

Accelerated solvent extraction—An efficient tool to remove extractives from tree-rings

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ABSTRACT

Prior to performing stable isotope analysis in tree rings, investigators usually extract cellulose from wood samples, which represents a tedious and time-consuming task. In this experiment, two different protocols for holocellulose extraction were compared, namely the Jayme-Wise technique and the Accelerated Solvent Extractor (ASE), a relatively new device operating under high temperature and pressure. We found that both techniques are equivalent regarding resin removal, produce comparable $\delta^{13}C$ results, do not damage the samples, and leave no resin in the xylem rays after treatment. However, the ASE is a lot less time-consuming, being ten times faster than the soxhlet based method, in addition to being safer and more convenient.

1. Introduction

Tree rings are commonly used as proxies for past climates (Dean, 1997; Hughes, 2002). Providing an adequate cross-dating of samples, they guarantee an access to an annual time resolution and allow for the creation of long, centennial to millennial chronologies (Hughes, 2002). Dendroclimatic proxies can be either structural (e.g., ring widths or wood density) or geochemical (e.g., stable isotopic composition of carbon, oxygen, hydrogen or nitrogen (McCarroll and Loader, 2004; Doucet et al., 2012). Among the geochemical proxies, $\delta^{13}C$ analysis is increasingly used as a high-resolution climate proxy, due mainly to the evolution and affordability of mass-spectrometers. When performing spectrometry analyses to track annual changes in tree ring $\delta^{13}C$, cellulose is commonly isolated at various levels of purity (i.e., holocellulose and its two components: hemi-cellulose and alpha-cellulose). This is because whole wood contains variable amounts of oils, resins and lignin which are isotopically different from one another (Olsson et al., 1972; Wilson and Grinsted, 1977). Moreover, while constructing millennial chronologies, the comparison of $\delta^{13}C$ measurements might be complicated because modern and subfossil wood have differential resistance to diagenesis. By opposition, cellulose is abundant in tree trunks and stable isotope ratios are relatively stable over time (Savard et al., 2012). Once formed, cellulose cannot be translocated in the tree (Leavitt and Danzer, 1993; McCarroll and Loader, 2004).

Among holocellulose extraction methods, solvent-based ones are the most time consuming (Gaudinski et al., 2005). With a traditional soxhlet extractor, two days must be counted (Leavitt and Danzer, 1993), sometimes even more, to prepare suitable samples for spectrometric analyses. In order to hasten the process, researchers often pool all the rings from the same year, but from different trees (Robertson et al., 2008). Here, we demonstrate that extracting holocellulose can be facilitated using the Accelerated Solvent Extraction (ASE) technology. The ASE instrument performs the extraction of resins and other impurities under high temperature and pressure in a considerably shorter amount of time and holds great promise for the processing of numerous samples as

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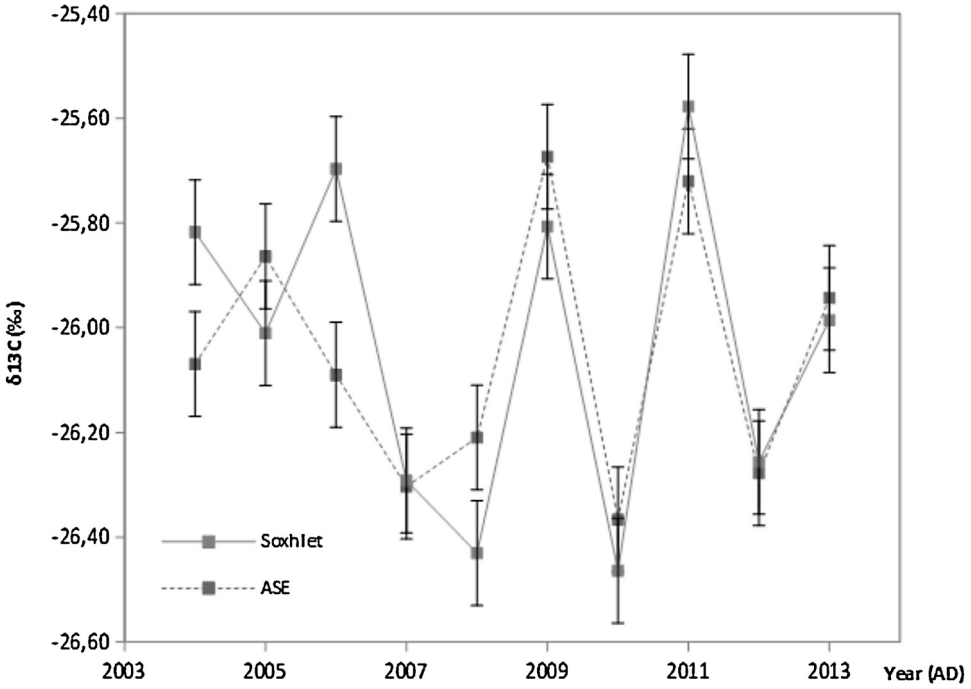

Fig. 1. Schematic ASE process

required to establish millennial-scale time series. Although limited studies already used the pressurized extraction to analyse stable isotopic ratios in cellulose (e.g., Miller, 2005), no exhaustive comparison between the two methods has been carried out until now. Such is the aim of the present study.

2. Methods

A mature (113 years) living black spruce (*Picea mariana* Mill) was sampled on September 5th, 2013 near Radisson, eastern James Bay, Canada (N 53°31′/W 77°38′). Ten rings spanning the 2004–2013 period were individualized and sliced in half radially for soxhlet and ASE extractions, respectively. Each half ring was milled, and carefully weighed before being sealed in a glass fibre pouch.

Soxhlet extractions were performed following the protocol of Leavitt and Danzer (1993). For the ASE extraction, the samples were inserted in a 66-ml cylindrical cell, placed in the chamber of a Dionex ASE-150 extractor (Fig. 1). The chamber was heated at a temperature of 100 °C. A static valve then closed and solvent was pumped at high pressure in the cell. This step is referred to as static extraction. Its duration may vary with the equipment and the extraction parameters used, but it is usually shorter than 20 min (Richter et al., 1996; Giergielewicz-Mozajska et al., 2001; Kettle, 2013). When the cell's pressure reached 1700 psi, the static valve unlocked to evacuate the fluid in a designated vial and the samples were rinsed with fresh solvent. The static extraction cycle can be repeated several times, if needed. When the last extraction was completed, the whole system was purged with nitrogen to remove the remaining solvent in the cell and tubing (Giergielewicz-Mozajska et al., 2001).

For both techniques, extraction was first performed with a 3:1 toluene/ethanol solution and, second, with pure ethanol (99% or 100%). Then, all samples underwent a series of additional treatments: a six hour hot water immersion, a sodium chlorate and acetic acid bleaching to remove lignin and finally all samples were rinsed with deionized water. $\delta^{13}C$ analyses were performed at the GEOTOP centre (UQAM) using an Isoprime100^{TM} continuous flow

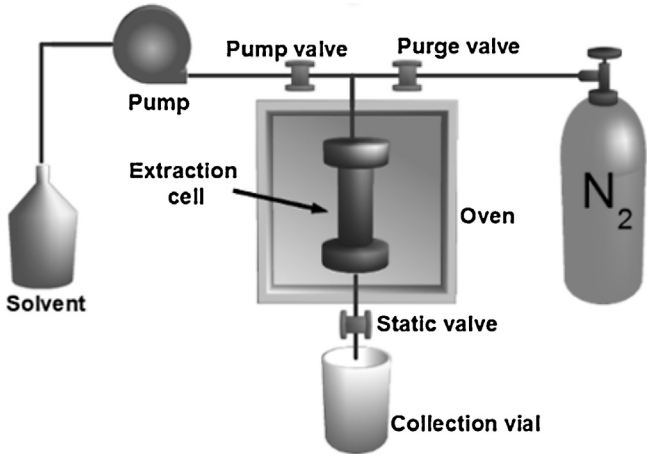

Fig. 2. ASE vs Soxhlet-treated $\delta^{13}C$ measurements