Secrets IN THE WOOD

For centuries, luthiers have suspected that the spruce and maple used by Antonio Stradivari had special qualities. A recent series of experiments has sought to confirm or deny these suspicions, and lead researcher **Hwan-Ching Tai** explains the methodology and findings

COURTESY CHI MEI MUSEUM, TAIWAN

Any serious attempt to recreate the merits of Stradivari instruments has to begin with sourcing the right wood. This means Norway spruce (*Picea abies*) for the top, and maple (several *Acer* species) for the back. However, even after a century of intense scientific investigations we still do not understand the detailed molecular composition and structure of Stradivari's wood. To complicate the matter further, his wood has undergone additional transformations, either by the maker himself or from the subsequent centuries of playing the instruments. This article will discuss why undiscovered secrets could still lie hidden within these wooden masterpieces made by Cremonese luthiers, and how this Pandora's box might be unlocked through chemical investigations of wood.

The only historical clue about the source of Stradivari's wood comes from the maker's grandson Paolo, who stated in 1775 that the spruce was purchased from Brescia from one Signori Banchetti, as described in Stewart Pollens's 2010 biography of Stradivari. This makes historical sense because Brescia was producing violins almost as early as Cremona, and Brescia is closer to the Alps, the only source of *Picea abies* around Italy. If Paolo's accounts were correct, then Stradivari's spruce could have come from the central or eastern parts of the Italian Alps. Nowadays, the region around the Fiemme valley in northern Italy is often claimed to be the source of his spruce. Wood from this region could be transported along the Adige river to enter the Po valley at Verona. The major road from Verona to Cremona would pass through Brescia. It is therefore plausible that Stradivari bought resonant spruce originating from the Fiemme valley in the southern Tyrol, which was inhabited by German-speaking people. Other theories suggest that spruce from the western Alps could also reach Cremona by transportation along the Po river. Future advances in dendrochronology may eventually help us locate the Alpine forests producing Stradivari's spruce.

As for Stradivari's maple, it is generally believed that the plain type came locally from Italy and the curly type came from the Balkan peninsula. 'Curly' maple is not a particular tree species, but a type of wood figure found in different maple species. Many sources claim Stradivari's maple to be *Acer pseudoplatanus* (sycamore maple), *Acer platanoides* (Norway maple) and *Acer campestre* (field maple). However, it is impossible to determine the exact species from the wood figure alone. It is possible that advanced wood DNA testing of core samples may be used to determine the exact maple species, but there appears to be no compelling reason to invest so much effort. Simone Sacconi believed that plain maple and curly maple both made equally excellent violins, and the higher price of curly maple was associated with the more expensive instruments for rich clientele. ▹

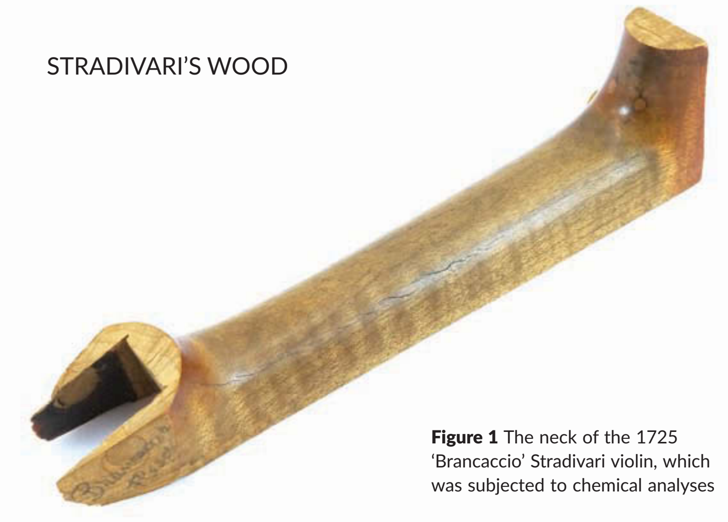


Figure 1 The neck of the 1725 'Brancaccio' Stradivari violin, which was subjected to chemical analyses

Although modern makers can still purchase tonewoods with natural qualities comparable to those in the wood used by Stradivari, there are three additional factors that may subsequently alter the wood properties in Stradivari instruments. These factors are: artificial wood treatments; age-dependent chemical transformations; and the effects of long-term vibration. The only visible traces of such changes may be the yellowing of wood, while other changes will require special scientific instruments to detect.

I recently headed a study, published in the January 2017 issue of the *Proceedings of the National Academy of Sciences*, in which a team of chemists and instrument specialists analysed maple shavings from instruments that had undergone repair to the back plate. These were a Stradivari violin (1717), two Stradivari cellos (1707, 1731) and one violin by Guarneri 'del Gesù' (1741). The instruments were provided by Joseph Nagyvary/the late René Morel, and by Guy Rabut/Brigitte Brandmair. The Chi Mei Museum in Taiwan generously provided the neck of a 1725 Stradivari violin, from which previously untouched wood materials were retrieved (**figure 1**).

There are three types of organic fibres in the wood: cellulose, hemicellulose and lignin. Our first test was to quantify these components using solid-state nuclear magnetic resonance (NMR), which detects carbon atoms from different organic molecules. NMR spectra of historical samples showed signs of lignin oxidation, the predicted consequence of which would be the yellowing of wood, which was apparent to the eye. More importantly, we detected the decomposition of one-third of the hemicellulose after 300 years. This was clearly observed in all historical samples, providing independent confirmation of their age. Its predicted consequence is reduced moisture absorption, because of all three components, hemicellulose is the one that absorbs most moisture from the air.

We measured the equilibrium moisture content of the wood by placing 5mg of powder on an electronic balance, accurate to 0.1μg. By heating the sample from 35°C to 150°C, essentially all moisture was driven off, and the weight loss corresponded with the absorbed moisture. On average, Stradivari's maple absorbed 25 per cent less moisture than modern maple. Reduced moisture content in wood generally means greater mechanical strength and less vibrational damping. Many violin and bow makers have long believed that aged wood becomes harder and drier, and our data appeared to support their views.

Another potential consequence of hemicellulose degradation is reduced molecular adhesion between the cellulose and the lignin. This appeared to be more serious in Stradivari's violins than in his cellos. As the wood samples were heated from 150°C to 600°C under air, controlled combustion took place and heat was released. The heat-release profile (**figure 2**) showed two peaks for modern maples and Stradivari cellos. His violins, however, exhibited an extra peak only previously seen before in fungus-degraded wood. This extra peak implied some sort of molecular detachment between lignin and cellulose. Because this extra peak was only observed in Stradivari's violins but not his cellos, it may have been caused by high-frequency vibrations (**figure 3**).

Cellulose fibres exist in two states in the wood: crystalline and amorphous. These form alternating domains along the fibre axis. We wanted to establish whether the static loading force or the vibration had reduced the amount of crystallinity (the 'crystalline/amorphous ratio') in Stradivari instruments, which would reduce the mechanical strength and service life of the wood. By X-ray diffraction, we found no change in the crystallinity of cellulose in historical instruments, which is good news for their preservation.

Although our data suggest that ageing and vibration are two critical factors that contribute to chemical changes in Stradivari's maple, there still remains the third factor, which is also important – namely artificial wood treatments, such as boiling, steaming, soaking, fuming, sunlight, and the application of chemical substances. All of these could have led to chemical alterations in the wood. Some treatments might have left detectable traces, while others may be undetectable using today's scientific instruments. In this study we conducted elemental analyses to find out if there were signs of chemical treatment. By dissolving ▹

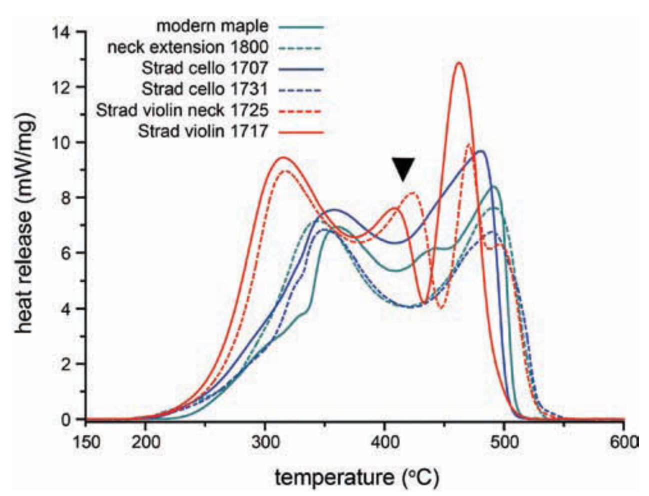


Figure 2 Oxidation thermograms of historical maple specimens. The black arrow indicates the extra peak only found in Stradivari violin samples

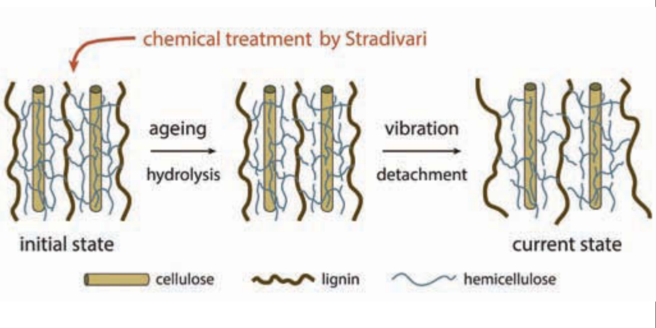


Figure 3 The combined effects of ageing and high-frequency vibration loosen wood fibres in Stradivari violins

'BRANCACCIO' NECK PHOTO COURTESY CHI MEI MUSEUM, TAIWAN

The 600MHz nuclear magnetic resonance spectrometer used to analyse wood fibres at the Department of Chemistry, National Taiwan University

wood samples in nitric acid, followed by vaporising with a plasma torch, the atomic ions in each sample were detected using a mass spectrometer. This gave us their elemental profiles. Not all of the elements in the periodic table could be detected simultaneously, and our examination was mostly directed towards the metallic elements of potential relevance. The 1731 Stradivari cello and the violin neck both showed elevated levels of sodium, potassium, calcium, zinc and copper. The remarkable consistency in the elemental compositions between these two samples implied that they probably originated from the same batch of wood.

However, there is no straightforward interpretation for these elemental changes. For example, since our analysis could detect neither chloride nor carbonate ions, we could not tell if the sodium came from sodium chloride or sodium carbonate. Even if it were sodium chloride, it could have originated from immersion in seawater, an artificial salt bath, or from the sweat of players' hands. Judging from the amount of sodium detected, as well as the changes in other elements, we thought that soaking in a salt bath was quite likely, but that would be indistinguishable from repeated surface applications of salt solution. We suspected that the potassium came from wood ash, and the calcium from lime, which were alkaline substances suitable for wood treatment. The copper and zinc could have been blue and white vitriols applied to kill worms and fungi. But frankly, these were not the only plausible explanations. Even if we assumed

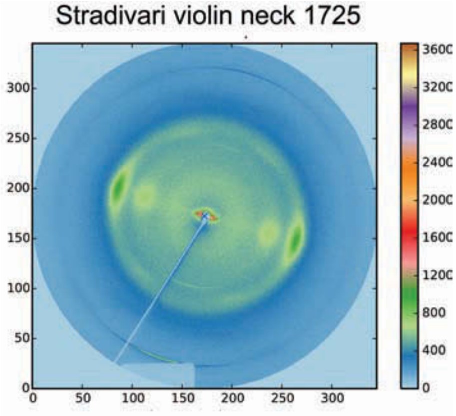
STRADIVARI VIOLINS MIGHT LOSE THEIR SIGNATURE BRILLIANCE OWING TO WEAKENED CELL WALLS

correctly, we still do not know the pH of the lime solution or the duration of soaking; and we cannot say whether these minerals were applied at higher concentrations first and then washed off, or if the wood was first boiled or baked. There is insufficient analytical information for us to reconstruct the original treatment protocol. At best, our analytical evidence offers some clues about the existence of artificial chemical treatments.

Without knowing the exact nature of the artificial treatments applied to Stradivari's maple, it is difficult to tell if such treatments could influence its acoustics or preservation. Nor could we directly measure the mechanical properties of wood from very small historical shavings. Moreover, artificial treatments may interact with the effects of ageing and vibration over several centuries, creating complex and unexpected results. In our experiments we observed that Stradivari violin specimens showed somewhat more hemicellulose degradation than his cellos. There are a number of possibilities that may lead to this difference: the preferential boiling of violin plates, the longer soaking of violin plates in alkaline solutions, the effect of high-frequency vibration, or statistical coincidence. Any of these interpretations can only be considered as speculative at this point.

For the past two centuries, standard practice for luthiers has been to cut down the spruce and maple and let the tonewood air-dry for several years before making instruments. Evidently, this was not the case for Stradivari's maple. Its peculiar pattern of elemental changes did not fit well with trivial explanations such as ponding, river transportation of lumber, accidental contamination or soil conditions. We do not know how, why, and by whom the chemical treatment was conducted. Moreover, the spruce plates of Cremonese instruments have never been analysed by modern chemical methods, and hence we have no idea what hidden properties may be found therein.

So far, only a few antique maple specimens of non-Cremonese origin – an English viola, a French violin, and an Italian neck modification – have been tested for wood mineral treatments. All the tests turned out negative. There were also no written accounts about the mineral treatment of wood for violin making passed down by traditional violin makers in Europe. To clarify whether mineral wood treatment was an exclusive secret of Cremonese masters, we need to analyse instruments from other Italian cities (such as Venice and Naples) from around the early 1700s, as well as from other Cremonese families (such as Amati and Rugeri).



X-ray diffraction pattern from the maple shaving of the 1725 Stradivari violin neck

Examples of modern violin backs made with plain maple (*left*) and flamed maple (*right*)

Maple shavings from the 1731 Stradivari cello

Although we still do not understand the actual formulation and procedure of mineral treatments for Cremonese maple, some educated guesses can be made about their possible purposes and effects. First, zinc and copper are known to offer protection against fungi and worms, and hence some minerals may act as wood preservatives. Second, sodium chloride and many common minerals absorb moisture from the air, so their presence in the wood helps retain moisture in cold and dry weather, preventing excessive shrinking and cracking. Third, the soaking of wood in certain chemical solutions, such as dissolved wood ash or lime, could help remove sap residues, resin acids and tannic acids along with other wood components. Prolonged alkaline treatment may even cause hemicellulose decomposition.

Judging from our data, the degradation of hemicellulose will continue naturally with ageing, and additional vibration will promote molecular rearrangement as the hemicellulose breaks down. It may be anticipated that after another century or two, the wood in Stradivari violins will have different molecular and structural properties from those it has today. Its acoustic properties will also continue to evolve, but we do not know if the change will be for better or for worse. In the worst-case scenario, Stradivari violins might lose their signature brilliance owing to weakened cell walls, judging from how ancient examples of the Chinese *guqin* have tended to develop rounded tones after 500–1,000 years. It remains to be investigated if the introduction of divalent and trivalent metal ions can promote molecular crosslinking to compensate partially for the structural breakdown. The decision to keep the 'Messiah' Stradivari and the 'Cannon' Guarneri 'del Gesù' being played as little as possible may be a good idea from the conservation perspective.

Finally, some words of caution should be given about violin makers experimenting with various wood treatments. Baking, steaming, boiling and the use of acidic solutions, basic solutions and UV illumination (often accompanied by ozone generation) can easily lead to excessive hemicellulose and/or lignin degradation if not carefully controlled. Such damage may result in brittle woods that develop irreparable cracks after just 10–20 years of playing. On the other hand, mechanically vibrating new wood with a playing-in device may not achieve the same effects as playing for 200 years, because the latter is accompanied by the gradual decomposition of hemicellulose. This creates some loose space between wood fibre molecules, giving the molecules more room to rearrange. Without careful planning and quality control based on scientific analyses, experiments aimed at accelerating wood ageing may do more harm than good.

Making instruments with old wood from buildings and furniture is also likely to be counterproductive, and the Hills advised against it. As a rule of thumb, only one tree in a hundred can make quality tonewood. The chances of finding such superior wood in buildings and furniture are extremely low. Among the 300-year-old spruce samples from old European buildings that we recently tested, two out of three showed severe loss of cellulose crystallinity in X-ray diffraction experiments. Wood suffering from such structural breakdown, perhaps owing to stress loading and weathering, will only create failing buildings and violins.

Using air-dried tonewood without special treatment has been the gold standard in violin making for 200 years. Many fine instruments have been built this way, delivering reliable performances over multiple generations. To venture beyond this, we must further analyse the chemical distinctions between Stradivari's wood (in its current state) and modern tonewood, and ensure that our experimental efforts are really bridging the critical gap, instead of creating damaged goods. We are now planning a series of new experiments to analyse more antique maple specimens and apply additional spectroscopy methods (infrared, Raman, auto-fluorescence, terahertz, second and third harmonic generation) and structural examination (using electron microscopy and small-angle X-ray scattering). Spruce shavings from Cremonese instruments are also being analysed.

Even with all this forensic archaeology, it will be impossible to reconstruct scientifically how tonewood was harvested and processed three centuries ago, or to understand fully the molecular changes due to ageing and vibrations. Nevertheless, the more we learn through analytical science, the better we will be guided in terms of conducting new wood experiments for 21st-century instrument building, not only for violins but also for stringed instruments across many cultures. ●