RADIOCARBON LABORATORY

SAMPLE PROCESSING

What is "pretreatment"?

Although it sounds like something that ought to come before the treatment, pretreatment it the term that is customarily used to describe the processes used to isolate the required carbon fraction from a sample for radiocarbon dating. In most cases, the desired fraction is carbon from molecules indigenous to the organism when is was alive, and isolating it means removing any contaminating organic materials that may have been introduced later.

Summary of Pretreatment Procedures

Physical pretreatment: The first step for all samples submitted to the laboratory is physical examination and cleaning. It may seem obvious, but identification labels and descriptions are examined carefully to insure that what we are about to analyse is what the submitter thinks she has submitted. This is not a trivial step:

- A textile may be made of more than one type of material.
- Charcoal may prove to be degraded and oxidized plant fragments.
- Shells may have a powdery/chalky appearance, indicating recrystallization.
- Sediments may be submitted which, when examined under the microscope, turn out to be a mixture of soil, flecks of charcoal, fragments of wood and plant debris. Each of these components was deposited in the sediment from a different origin and possibly could have different ages.

In each of these cases, we would report our observations and discuss with the submitter which fraction is the most optimal for dating based on her research objectives. Because the sample size requirement for AMS is so small, it is possible that different fractions within the sample can be separated, dated independently and the ages compared.

During physical pretreatment, samples are examined under a microscope. Obvious extraneous materials such as rootlets or thread are picked out with forceps. Surface dirt and contamination such as glue or ink is removed. Exterior parts of the sample are washed or otherwise cleaned as appropriate for the type of sample. Some samples are sieved to select an appropriate size fraction. Finally, the sample is crushed or ground to reduce it in size and increase the surface area.

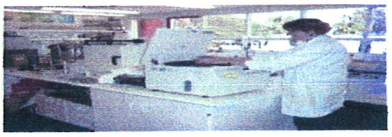
Chemical pretreatment:

The objective in chemical pretreatment is to remove any contaminants in the sample that can be made soluble by heating in a series of solvents. While pretreatment procedures are standardized according to our QA manual, they must also remain flexible to take into account the varying condition of the samples submitted to the laboratory. There are variants depending upon both the condition and size of the sample. For example, wood may have the cellulose extracted or be treated with the A/A/A method. For some samples, sodium pyrophosphate is added to the sodium hydroxide in the alkaline solution to help deflocculate clays for easy removal. If there is reason to suspect that not all the contaminants were removed, a step may be repeated or the concentration of a solution increased.

The following are pretreatment procedures for the most common materials submitted to the laboratory. The list is by no means exhaustive and numerous pretreatment strategies exist. If you want information on the pretreatment of a sample type that is not on this list, please contact us.

Charcoal, plant material, degraded wood:

After physical pretreatment and removal of any rootlets or visible contamination, these types of sample materials are pretreated with what is termed the Acid/Alkali/Acid (A/A/A) method. In A/A/A, the sample is heated in 0.5M HCl, filtered, rinsed, heated in 0.1M NaOH, filtered, rinsed, and finally heated a last time in 0.5M HCl, filtered, rinsed with dH_2O and dried.



Soils, sediment, peat:

Two different methods my be used for treatment of soils, sediments and peats.

- Total Organic Carbon (TOC) removes only inorganic carbon and absorbed CO_2, leaving the entire organic carbon fraction.
- Acid/Alkali/Acid (A/A/A) treatment removes all but the least mobile organic fraction, leaving the "humin" fraction only.

In ordinary situations, A/A/A is the preferred method of treatment, but sometimes researchers studying the movement of carbon in soils prefer to date the TOC fraction or the humic acid fraction. For separation and analysis of the complex cycling of Soil Organic Matter (SOM), specialized pretreatment procedures exist (c.f. Trumbore and Zheng 1996; Leavitt et al. 1996).

TOC:
the sample is heated in 0.1M HCl, then freeze-dried.

A/A/A:
the sample is heated in 0.5M HCl, filtered, rinsed with dH_2O, heated in 0.1M NaOH/0.1M $Na_4P_2O_7$, filtered, rinsed with dH_2O, and finally heated a last time in 0.5M HCl, filtered, rinsed and dried.

Humic acid precipitation:
the sample is heated in 0.5M HCl, filtered, rinsed with dH_2O, heated in 0.1M NaOH and filtered. The NaOH filtrate is collected. Humic acids in solution are precipitated out with the addition of 6M HCl. The precipitate is collected, redissolved in NaOH, then reprecipitated with 6M HCl, and dried.

Wood - cellulose extraction:
The cleaned ground wood is heated in 0.5M HCl, filtered, and rinsed with dH_2O to neutral. It is then heated in 0.1M NaOH, filtered, rinsed with dH_2O and repeated. After the second NaOH step the residue is heated in a 4% solution of H_2O_2 at pH 11. This step is repeated until the residue is bleached, then it is filtered, rinsed with dH_2O. Finally, it is heated again in 0.5M HCl, filtered, rinsed in dH_2O and dried.

Textiles
Textiles submitted to the laboratory vary in their degrees of preservation. Old wool for example may be quite degraded and readily hydrolyse in alkaline solution. The cellulose of cotton will usually sustain a more vigorous treatment and large samples of hemp or other cellulosic fibers may even be subject to cellulose extraction method described above. In general, the purpose of pretreatment of textiles is to remove dirt, grease, fats and oils, and dyes or coloring agents, if soluble.

Depending upon the condition of the fibers, textiles go through the following sequence: after physical cleaning and shredding into small fibers, the sample is heated in hexane, filtered and dried, heated in isopropanol, filtered and dried, heated in acetone, filtered and dried. The residue is then treated with a series of acid/alkali/acid washes with 0.1M HCl and 0.1M NaOH, rinsed thoroughly with dH_2O, and dried.

Bone
After examination and physical cleaning, ground bone powder is demineralized with 0.5M HCl until carbonates are dissolved. The rough collagen is rinsed to neutral and converted to gelatin in hot 0.01M HCl in an inert atmosphere. The gelatin is then filtered twice, and freeze dried. Sub-samples of the gelatin may be taken at this time for stable carbon and nitrogen analysis and amino acid analysis, in addition to the AMS measurement.

Shell and other carbonates:
After physical examination and cleaning of the surface (and evaluating the need for X-ray diffraction), the surface of shells may be etched with a 0.1M solution of HCl, rinsed with dH2O and dried. CO_2 is produced from the carbonate through the addition of 85% o-phosphoric acid in a closed, evacuated glass vessel.

After a sample has been pretreated, it is ready for the next stage in the dating process: combustion. When organic materials are burned in oxygen, the carbon is converted to carbon dioxide (CO_2) with water and often other compounds as by-products of the reaction. The sample CO_2 can be used in gas proportional counting or converted to benzene for LSC decay counting. For AMS dating, the CO_2 is converted to graphite.

Combustion
In the combustion stage of sample processing, carbon dioxide (CO_2) gas is produced from the pretreated residue of samples and purified for graphitization. Samples are combusted at 900°C for 2 hours in evacuated, sealed quartz tubes with cupric oxide and silver wire. The cupric oxide provides oxygen for the combustion and the silver isolates sulphur and halogens in a solid form. After combustion, the CO_2 is cryogenically purified by passing it through dewars of ethanol/dry ice to trap

water. The purified CO_2 is collected in a glass vessel for transport to the graphitization and mass spectrometry laboratories.

Graphitization

The final step in sample processing is the conversion of the sample CO_2 to elemental carbon graphite. In the graphitization laboratory, the sample CO_2 is mixed with a stoichiometric amount of hydrogen gas inside a glass reaction vessel. The reaction vessel contains a small amount of iron powder which will act as a catalyst for the reaction. The reaction vessel is placed in a 700° C furnace and in about 5 hours the CO_2 converts to graphite. Water is trapped out as a by-product of the reaction.

Stable isotope measurements

It is standard procedure to measure $d^{13}C$ on all samples, using conventional mass spectrometry. The cost of this is included in the overall price of the AMS measurement. Note: the $d^{13}C$ value is measured on the CO_2 gas resulting from the sample combustion, and is required for correcting the radiocarbon result for isotopic fractionation. While generally it will closely reflect the stable isotope ratio in the parent sample, we do not warrant it as an accurate estimate of this quantity.