

Archaeological Preservation Research Laboratory Report 11:

**Mass Spectrographic Analysis of Out Gasses Created From the
Dehydration of Archaeological Wood Samples**

C. Wayne Smith

D. L. Hamilton

Conservation Research Laboratory/Archaeological Preservation Research
Laboratory

Texas A&M University

Advances in passivation polymer research at the Conservation Research Laboratory (CRL) have necessitated an accurate determination of how various forms of dehydration affect bulking and polymerization processes applied to the preservation of waterlogged archaeological wood. Prior conservation, waterlogged wood samples are rinsed in a series of fresh water baths to remove as many soluble salts from the wood as possible. After cleaning, the wood is then dehydrated in a series of alcohol/acetone baths prior to bulking and consolidation. In some cases cold vacuum dehydration, accomplished by the exchange of water for acetone in a freezer-mounted vacuum chamber, has been employed at the CRL to reduce shrinkage in severely waterlogged wooden artifacts. Qualitative tests such as silver nitrate testing and quantitative tests such as titration are often used to determine the point of optimum rinsing and desalination.

Experience has indicated that two factors are important for conserving organic materials with silicone oils. While it is not necessary to eliminate all water from an artifact, it is essential to remove as much of the free-moving water as possible. Acetone is easily driven from samples in a vacuum chamber so, a dehydration process that effectively causes a higher output of volatile vapors should also facilitate a more effective exchange of silicone oils to replace the acetone. To evaluate which processes of dehydration are potentially suited for conservation practices utilizing silicone bulking techniques, a test was devised to study collected gases from dehydrated samples using electron ionization mass spectrographic analysis to produce a spectrographic analysis of the off-gasses from waterlogged archaeological wood samples. The five most commonly used dehydration processes at the Conservation Research Laboratory are represented in the chart below (Table 1).

Table 1. Commonly used dehydration processes.

Dehydration Process	General Steps in Process
A. Acetone	Series of baths of fresh acetone to remove water
B. Alcohol/Acetone	Working through a series of alcohol baths followed by acetone baths to remove water
C. Acetone/Vacuum/Freezer	Series of acetone baths under vacuum at 0 C
D. Alcohol/Acetone/Freezer/Vacuum	Alcohol-acetone baths under vacuum at 0 C
E. Acetone/Warm out gassing / Vacuum	Series of acetone baths at ambient pressure and then out gassing at 145 F until surfaces are dry

Electron ionization (E.I.) mass spectra of the out gasses from the five waterlogged wood samples were acquired on a VG Analytical 70S (Manchester, UK) high resolution, double focusing, magnetic sector mass spectrometer. The VG 70S was equipped with a VG 11/250J data system that allowed computer control of the instrument, data recording, and data processing. The E.I. source was maintained at 220 C during the analyses while 70 eV positive analyte ions were extracted and accelerated to 8 keV and then mass analyzed. Gaseous samples were collected in a one liter glass bulb and were allowed to leak into the mass spectrometer using a regulated inlet. Liquid samples were analyzed by injecting 2 μ L on the sample into a heated reservoir maintained at 180 C. The sample was then allowed to leak into the mass spectrometer through a glass jet. Approximately 15 mass spectra were taken and averaged per sample and then the average ion abundance per sample was reported. Background measurements of water ($m/z+18$) were determined to be approximately 1 mV at the amplification used to collect the analyte mass spectra.

The first method of dehydration is to simply immerse the waterlogged wood sample in a series of fresh acetone baths, allowing adequate time for each bath to draw free-flowing water from the sample. Because of the small sample size used in this experiment, sample A was placed into a beaker containing 500 milliliters of fresh acetone and allowed remain at room temperature for 24 hours. The sample was then placed into an identical volume of fresh acetone and allowed to sit undisturbed for an additional 24 hours. After this period of dehydration, the sample was then removed from the acetone bath and lightly surface tamped with a dry paper towel to remove excess acetone from the sample's surface. Additional acetone was allowed to out gas from the sample by allowing it to sit on a dry paper towel for two minutes. The sample was then placed into a clean beaker containing 300 milliliters of PR-10 silicone oil and then the beaker was immediately attached to an in-line gas trap assembly which in turn was connected to a vacuum pump. Liquid nitrogen surrounding the trap assembly was used to freeze the entire range of gases being given off by the sample under a vacuum of 28 Torr. After twenty minutes of applied vacuum, the contents within the gas trap were collected and placed into sterile specimen vials for transport to the mass spectrometer for analysis.

The second waterlogged wood sample (sample B) was dehydrated in much the same fashion as sample 1, except that for initial dehydration, it was placed into a beaker containing 500 milliliters of ethanol and allowed to stand for 24 hours at room temperature. After this first bath, the alcohol was replaced with 500 milliliters of fresh acetone and after capping to prevent evaporation, it was allowed to sit at room temperature for an additional 24 hours. Like sample A, sample B was then removed from the bath and surface tamped with dry paper towels to remove pooled acetone from the surface and then placed on a dry paper towel and allowed to continue out gassing for two minutes. At this point, the sample was then quickly placed into a clean beaker containing 300 milliliters of PR-10 silicone oil and like sample A, hooked in line to a gas trap and vacuum pump. Liquid nitrogen, surrounding the trap assembly of the gas trap, was used to freeze and capture out gases from the wood sample for analysis.

Waterlogged wood sample C was dehydrated using a series of acetone baths that were placed in a freezer mounted vacuum chamber as a means of determining if the combination of low temperature and vacuum has a significant effect on the dehydration process. Sample C was placed into 500 milliliters of fresh acetone and placed into the freezer mounted vacuum chamber where it remained under a vacuum of 28 Torr for 24 hours. After 24 hours, the wood sample was rapidly transferred to a clean beaker containing 500 milliliters of fresh acetone and then returned to the freezer vacuum chamber for an additional 24 hours of dehydration using the same vacuum pressure as before. Upon completion of the second acetone bath, the sample was removed from the freezer and surface patted using dry paper towels. After out gassing on a dry paper towel for two minutes, the sample was quickly placed into a clean beaker containing 300 milliliters of PR-10 silicone oil and then like samples A and B under a vacuum of 28 Torr for twenty minutes. Liquid nitrogen was used to freeze the products of out gassing from the wood sample under vacuum and like other samples, the frozen products of out gassing from the sample were collected and stored in a sterile, air-tight vial for analysis.

- A. Beaker with wood sample in silicone oil
- B. Vacuum line to gas trap
- C. Gas trap partially submerged in liquid nitrogen
- D. Container of liquid nitrogen
- E. Vacuum line to vacuum pump

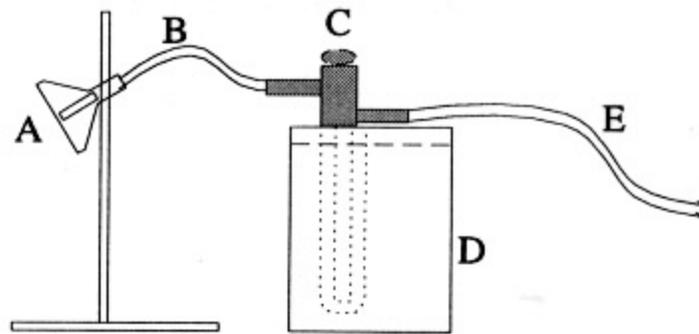


Figure 1. Setup showing beaker and gas trap assembly mounted in liquid nitrogen.

A fourth sample, D, was dehydrated utilizing the method used for sample C, except that instead of two acetone baths under vacuum, initial dehydration was started using ethanol so that after 48 hours, the sample had been dehydrated in one bath of alcohol and one bath of acetone. After collecting out gasses from the sample using the same apparatus and methodology as were used for the other samples, the vial was stored in a freezer until all the samples were prepared.

Silicone oil is not a volatile substance and because of its chemical purity, it was determined that it might be an ideal inert substance in which to immerse the wood samples during the out gassing process. To test this, an additional wood sample, sample E was dehydrated in two successive baths of 500 milliliters of fresh acetone at room temperature and then placed into a clean beaker where it was warmed at 145oF until all the surfaces of the wood sample were light brown in color (Figure 2). At this point, simply touching the outer surfaces of the sample indicated that it was dry although the weight of the sample indicated that the interior was still heavy with liquid. Like all of the

other samples, out gasses from sample E were collected in a liquid nitrogen cooled gas trap for a period of twenty minutes. After the products of out gassing from the sample were placed into a sterile, sealed vial, all of the samples were analyzed.

- A. Beaker with wood sample - no oil
- B. Vacuum line to gas trap
- C. Gas trap partially submerged in liquid nitrogen
- D. Container with liquid nitrogen
- E. Vacuum line to vacuum pump
- F. Heat lamp - adjustable height
- G. Temperature probe

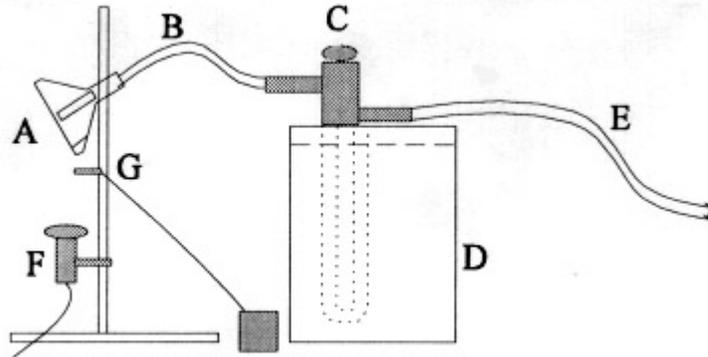


Figure 2. Basic set-up with heat lamp and temperature probe added.

Results

No attempt was made to evaluate the physical appearance of the five samples used in this experiment. Variability between samples is also another uncontrollable aspect of wood research. Although samples were all cut to the same size for testing (3cm long, 2 cm wide and .5 cm thick), differences in wood growth, degree of waterlogging, fungal and bacterial degradation as well as a host of other factors can expand the degree of variability between samples. Data from mass spectrographic analysis for each sample however, answers the basic questions of water replacement and mobility of volatile solvents within the samples. This data indicates significant differences in the relative intensity of elements collected during experimentation. Acetone used for this experiment was an industrial grade solvent which had been stored in a 55 gallon drum for approximately three months prior to use in this experiment.

Sample A was dehydrated using a sequence of two room temperature acetone baths, each lasting for 24 hours. Relative intensity of water, nitrogen, methyl and oxygen in this sample were the highest for all samples tested with amounts recorded as 2.5, 6.5, 25 and 2 respectively. The intensity of molecular acetone in this sample was approximately

equal to samples B, C and D, although the levels of molecular acetone were nearly doubled in sample E, which was warmed during out gassing.

Sample B was initially dehydrated at room temperature using a twenty-four hour alcohol bath, followed by an acetone bath. Recorded levels of nitrogen were approximately 50% less than those recorded for sample A while the levels of methyl and ethyl were reduced by approximately 66% and 50% respectively. Acetone levels in sample B were only slightly lower than those recorded for sample A.

Cold dehydration using successive baths of acetone and an applied vacuum to dehydrate sample C produced some interesting results. Analysis of the out gasses indicated that there was a nearly two-fold increase in methyl levels while nitrogen levels for this sample were the lowest of all samples tested, recording an intensity of 2.5.

Sample D, which was dehydrated in a sequence of cold alcohol and acetone baths under vacuum, registered increased levels of methyl and nitrogen (19.6 and 3.8 intensities respectively). Notably, the levels of acetone out gassing are substantially greater (32 intensity).

Sample E was warmed during the out gassing process and no immersion media such as silicone oil was used to support the sample during the gas collection process. Levels of volatile elements such as methyl, ethyl and acetone are predictably higher in sample E, although water out gassing from the sample is comparable to samples B, C and D. A lack of media to support the degraded cell structure of this waterlogged wood sample resulted in greater damage to this section of wood. Not surprisingly, the levels of out gassing methyl and ethyl are the highest in this sample and molecular acetone levels are 65% (53 intensity) higher than those recorded for sample D.

Trends

Sample E, which acted as a control for this experiment, served to indicate the maximum out gassing potential that might be expected for this group of wood samples. Because heat was used to accentuate the effects of out gassing, methyl, ethyl and acetone levels for the sample were the highest recorded. While less than the levels recorded for sample E, the levels for sample D were appreciably higher than out gassing levels recorded for samples processed at room temperature. A comparison of the relative levels of gasses from samples C and D is interesting because the higher levels of methyl and acetone gasses suggest that alcohol-acetone process dehydration may have been more effective in raising the overall levels of volatile vapor exchange, which suggests that this process may have a higher potential for exchanging silicone oils, or other bulking agents, into waterlogged materials.

With the exception of sample A, which registered water levels of 2.5, all of the other samples registered water levels of 2.0, which may suggest that from the standpoint of the removal of free water from waterlogged wood, all processes were relatively equal. Differences in bulking potentials then, lie in the heightened levels of volatile gases that

result in cold process, vacuum assisted alcohol-acetone dehydration . Table 2 includes the out gassing data for all five samples. Note that in all cases, the shaded acetone column is equal for all samples. We are suggesting that it is the rise in molecular acetone and methyl levels that makes two stage cold dehydration potentially more appropriate for silicone bulking.

Table 2. Data From Mass Spectrographic Analysis for Waterlogged Wood Samples.

	Nitrogen	Methyl	Water	C2H3	Ethyl
A	6.5	25.0	2.5	7.5	2.5
B	3.0	8.0	2.0	13.0	14.0
C	2.5	14.8	2.0	12.0	2.5
D	3.8	19.6	2.0	6.0	2.5
E	4.0	22.5	2.0	8.0	3.8

	Oxygen	C3H3	Acetone	Acetone	Acetone	Molecular Acetone
A	2.0	4.5	7.5	100.0	2.0	28.0
B	2.0	4.5	6.0	100.0	3.0	25.0
C	0.2	4.5	7.5	100.0	2.4	24.3
D	0.2	5.0	9.0	100.0	2.3	32.0
E	1.8	3.5	12.5	100.0	3.5	53.0

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