

NOTES AND COMMENTS

A DISCUSSION OF AN ALTERNATE APPROACH TO THE EVALUATION OF SAMPLE CONTAMINATION

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ABSTRACT. An approach to the evaluation of sample contamination based on the monitoring of contaminant removal during pretreatment is described. Spot tests and colorimetric reactions which could be adapted for this purpose are suggested.

There has always been concern in ^{14}C dating about the detection of sample contamination. Taylor (1980) proposed $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements as a possible means of evaluating sample suitability. However, by far the most common approach is the dating of multiple chemical fractions from a single sample. By comparing the ages obtained it is often possible to determine the nature of contaminants present and to select the most reliable age. The full potential of multiple fraction dating has been realized with the advent of accelerator mass spectrometry. Recent work described by Donahue, Jull, and Zabel (1984) on a single mammoth bone and Gillespie, Hedges, and Wand (1984) demonstrate the many and very specific fractions which can be isolated. However, this approach, while effective, is time consuming, labor intensive, and because of the multiple age determinations required, especially by AMS, quite costly.

Proposed here is an alternate approach to the same problem. The reason that contaminants cause anomalous dates is, of course, their incomplete removal during sample pretreatment. The approach proposed here involves the development of relatively simple and inexpensive techniques to detect potential contaminants in the untreated sample and to monitor the removal of these contaminants from the sample as pretreatment progresses. In this way, contaminated samples can be detected and appropriate treatment applied, before they are dated.

The ideal monitoring techniques for untreated samples would be simple spot tests applied directly to the solid material. Feigl and Anger (1966, 1972) provide a very thorough compilation of spot tests for both organic and inorganic compounds which could be adapted for this purpose. Some staining techniques used in plant and animal tissue microscopy could also prove useful; Humason (1979) and Johansen (1940) are comprehensive references on this subject.

For pretreatment processes, such as acid or alkali extraction, in which the datable fraction is an insoluble residue and contaminants go into solution, the best monitoring techniques would be colorimetric reactions which can be easily visualized and, if desired, quantified using relatively inexpensive colorimeters. The multiple volumes by Snell and Snell (1948-1970) are good sources of many colorimetric procedures.

In the case of the acid extraction of bone, eg, the dissolution of bone apatite and, by association, contaminating carbonates could be monitored by the colorimetric procedure for phosphates (AOAC, 1980).

Humic substances are another major contaminant that would require monitoring. The author briefly experimented with the use of the Folin-Denis phenol reagent (Folin & Denis, 1915) as a means of detecting humic acids because they were known to contain phenolic groups (Schnitzer & Khan, 1972, p 37). While preliminary results were promising, the reagent was subject to interferences from compounds such as ferrous ions (Snell & Snell, 1953, p 104) and additional work on the reliability of this reagent is needed.

A good monitoring technique must have two important features:

1) it must be sensitive to at least the parts per thousand range and ideally in the ppm range if very old samples are to be dated. For conventional dating this would require sensitivities in the mg and sub-mg range which is very common for the types of reactions proposed here. For AMS, μg and sub- μg detection limits would be needed and, while more difficult to attain, still feasible.

2) it must be reasonably specific for the contaminant of interest and must not be subject to interferences from inorganic or organic constituents, particularly the sample's datable fraction. Although even a non-specific reaction such as oxidation by chromic acid for the detection of total organic carbon (Graham, 1948) could prove useful for monitoring the extraction generally of any organic material.

Consider a hypothetical case to show how this approach could be used. An untreated sample is tested and contaminant A is found to be present. The sample is extracted, say in acid, to remove this contaminant and the presence of compound A in solution is monitored. This could be done by replacing the acid on an hourly basis until compound A was no longer detectable in solution, say, eg, after 4 hours. A minute amount of the insoluble residue present after this last extraction is tested for compound A and it is found to be absent, confirming the completion of the extraction. If compound A had still been present in the insoluble residue it would signal the need for more rigorous sample pretreatment, such as additional extraction with higher strength acid. In the absence of this monitoring, the incomplete removal of contaminant A might only have been recognized by an anomalous age.

In order to validate this approach to contamination monitoring, in test experiments it would be necessary to date multiple fractions of a single sample, for which AMS is especially suited. In the case above, eg, it would be necessary to date portions of sample acid extracted for say, 1, 2, 3, 4, 5, and 6 hours, respectively, to confirm that there is a correlation between monitoring technique and age. If the monitoring technique is valid, then the age of the sample should remain constant after 4 hours of extraction, if not sooner.

While the development and validation of monitoring techniques will not be an easy task, the approach described here will hopefully be found to merit further investigation.

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