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Tritium Effects on Plastics - Studies at the Savannah River Site

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Plastics are used in a variety of places in the tritium processing facilities at the Westinghouse Savannah River Company in Aiken, SC. Thus they are routinely directly exposed to tritium and suffer from radiation damage. This effectively limits their process lifetime as typically the properties that made them useful are adversely impacted. At the point where they must be replaced, they become radioactive waste. All radioactive waste is categorized and inventoried at the Savannah River Site (SRS), and a sound technical basis for this process is desired. Thus the Materials Test Facility of SRTC has embarked on a program to determine typical tritium content in waste plastics.

Initial work has focused on the plastic UltraHigh Molecular Weight PolyEthylene (UHMWPE). One use for this material is in valve tips of earthquake protection valves. Since these valves are normally open, the tip material sees varying but continuous tritium exposure over its service life. After considerable time (1-2 years) the tips blacken and harden and begin to leak, whereupon they are replaced. Several of these tips have been analyzed recently at SRS by dissolving and diluting samples of the tip material in water based solutions followed by subsequent liquid scintillation counting of the resultant liquid sample.

The exposed plastic tips examined so far have all shown extensive darkening and even across-the-face cracking. The plastic is embedded in a stainless steel holder for one type of valve tip, and must be removed to be analyzed. An Xacto knife is used for this, and it has been observed that the plastic is quite brittle. It will not so much cut out of the tip as break out in chunks. In addition a lot of fine and small flakes of material are produced as well. One type of tip has about 0.5-0.6 g of plastic in it, while a second type has a larger plastic piece weighing about 1.75 g.

The method places about .09 g. of irradiated plastic in a commercial Parr Acid Microdigestion Bomb (PADB). . The PADB consists of a stainless steel body fitted with a spring-loaded pressure relief plate. The sample is placed inside a Teflon liner that slips into the stainless steel body. A thermocouple is attached to the exterior of the PADB to measure its temperature.

About 3 ml of concentrated nitric acid is added and the sample is heated at 150 C for 2 (or more) hours. Less time has resulted in incomplete dissolution, especially with a sample composed of a few large chunks as opposed to the more usual powder/small chuck sample. The PADB is then cooled to body temperature and opened, and the liquid contents are transferred to a 1L volumetric flask. The Teflon liner is rinsed three times and the rinses added to the 1L flask. This solution is designated as the `mother liquor'.

At this point the original dissolution solution looks free of solid material, but does have some NOx gas visibly present. This disappears as soon as the sample is diluted to volume with deionized water. The Teflon liner shows an orangish color in the interior. The source has not been identified, but a nitration product is anticipated. With a 6 hour long dissolution, the orange color had penetrated to the outer surface of the liner, which is some 2-3 cm thick. This suggests a possible error if some T is lost to the Teflon. We have not yet assessed that magnitude of that error.

Subsequently 0.5 ml samples of the `mother liquor' are diluted to 1L, and 0.5 ml samples of those solutions are again dilute to 1L, giving a final dilution factor of four million. This highly diluted sample is then analyzed by an LSC technique where 1 ml of it is added to 20 ml of Ultima Gold AB cocktail, and that solution counted on a Beckman LL6000 LSC instrument for 15 minutes.

All of the sample preparation through the 1L dilutions are performed in a once-through air flow hood in the MTF. This hood is continuously monitored for airborne activity with Kanne detectors. The as received valve tips often show T release when first received. Working through the plastic extraction process, this activity tends to decrease with time. Eventually the fractured plastic tip can be left open in the hood with only slight airborne activity being noted. Typically, a spike of activity is detected when the PADB Teflon liner is opened after a dissolution. This quickly drops off as the sample is transferred to the 1L flask. However, some loss both before and after dissolution is experienced. Our best estimate of this loss is that it is on the order of 5 Ci total. Our current results indicate that the total T content of the small valve tips is 300-600 Curies.

Tritium incorporation into a process material like plastic can occur by three distinct pathways. The first is by simple dissolution of elemental tritium into the plastic. However, this tritium is expected to be quite labile and most likely is not present in the samples by the time they reach the MTF. The second method is by absorbtion of tritiated water into the plastic. This "HOT" water would slowly diffuse through the plastic and cause slow offgassing as the water reached the surface and evaporated. Thus depending on sample handling details, some of this material could show up in analyses. Finally, T can be directly incorporated in the -CH2- polymeric backbone through the effect of beta irradiation. The energetic beta particles could create free radicals in the polymeric backbone that would then react with either elemental T forms or with tritiated water. This tritium would not easily leave the polymer and thus forms the primary source of T that is detected in the analytical dissolution method. It is unknown if small samples taken from the tip would show homogenous incorporation or not.

We have repeatedly analyzed select samples to assess the analytical method's reliability. Sample results are presented as associated with a valve tip-sample code. This code is a four part one, and is described as follows. The first part is a simple internal designation (M1) of no significance at this time since all tips were presumed to come from the same site. The next part is the tip number (-1, -2, etc.). The next number is the sample number assigned to one of the .09 g samples. The final code (D3) indicates the results are from the third dilution, i.e. the sample that has been diluted 4 million times. Thus samples beginning with the same two codes (M1-2, M1-3) originate from the same tips.

We present below some current results. As can be seen, the reliability is not high at this time.

Sample	Analysis No.	dpm/ml	Sample	Analysis No.	dpm/ml
M1-2-2-D3	1	45800	M1-3-1-D3	1	130000
	2	108000		2	129000
	3	79800		3	29700
M1-2-3-D3	1	85600	M1-3-2-D3	1	132000
	2	63700		2	86900
	3	33400		3	46900

Most of these results are from multiple replicates. Within sets of replicates we have observed the majority of results to be consistent, but individual high values are observed. This kind of behavior (flyers) could be introduced by either an incomplete dissolution producing microscopic

particulates that appear in random samples, or by some kind of contamination problem. The samples are prepared with automatic pipettes using a new disposable tip for each sample. We have attempted analyses using a sample prepared separately in a cold laboratory from clean UHMWPE, and have observed no matrix effect. We have observed difficulties with flyers in similarly prepared tritiated oil standards. We have also compared a sample dissolved for 6 hours vs. the usual 2 hours and found the same problem in it. As of this date we have not isolated and identified the root causes for our lack of reproducibility. The difference between averages for a single tip could simply indicate inhomogeneous T incorporation in the tips.

We are pursuing two avenues to investigate this. First we are having the above samples rerun by a slightly different method in a second laboratory. Specifically we will be avoiding the use of the disposable tip pipette. Secondly, we are attempting to trap the posited particulates on filter paper. A 'tree' of horizontal filter papers has been constructed from Apiezon Q. The filter papers are supported by paper clips pressed into the sealing compound. Water from the samples, and clean water, is dropped onto the filter papers until they are fully wetted, but avoiding an excess that can cause the liquid to run off the paper. The papers are then left to air dry, whereupon the process is repeated several times. The intent is to leave behind non-evaporable plastic residue or particles on the filter paper. The filter papers will then be counted exactly as if they were smear samples. Any trapped particulates should clearly show up in that analysis.