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THE DETERMINATION OF CARBON-14 IN ACTIVATED METAL WASTES

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ABSTRACT

The inherent radioactivity and potential toxicity of nuclear waste, provide challenges to persons responsible for its characterization. Specifically, this paper describes the development of an analytical method to quantitatively measure ^{14}C in radioactive waste. A separation from other beta emitting isotopes is first required before the weak beta radiation of ^{14}C can be counted using liquid scintillation. Hence, this paper discusses the development of a modified, remote carbon analyzer which has provided a means to perform this separation. This modified technique is much easier than the difficult and time consuming techniques traditionally used for determining ^{14}C concentrations. The carbon analyzer (LECO® HF-400/IR-412 carbon analyzer) that was modified for remote operation in the Argonne National Laboratory-West (ANL-W) Analytical Laboratory Hot Cells (ALHC) has been used to separate and isolate ^{14}C from other beta emitting isotopes in samples of different matrices. These include irradiated beryllium from the Advanced Test Reactor located on the INEEL and samples of stainless steel that were irradiated in the Experimental Breeder reactor II.

INTRODUCTION

The isotopic characterization of radioactive waste is of great importance when considering the issue of long-term storage as required in the USA. The regulatory guidelines can be found in the US Code of Federal Regulation 10CFR 61.55 (1) and in the US Department of Energy Order 435.1 (2). Over all, there are four categories of radioactive waste as classified by federal law. They include: High-level, Transuranic, Uranium Mill Tailings and Low-level radioactive waste.

Out of the above listed categories, Low-level waste is a term that is rather misleading. “Low-level” radioactive waste does not necessarily imply “low radioactivity”. Basically, Low-level waste is classified by where it came from, not how radioactive it is. Therefore, it is defined as something that it is not, that is to say, it is not High-level waste i.e. fuel rods, nor is it Transuranic waste, nor is it Uranium Mill Tailings. The resulting broad category that comprises Low-level waste can range from protective laboratory clothing which may be only slightly contaminated, to used hardware from nuclear power plants which can be highly radioactive.

Since Low-level waste consists of such a diversity of radioactive 'types', it was necessary to subdivide this category into yet four additional groups according to the level of radioactivity of the waste material. These groups are named as follows: Class A, Class B, Class C, and Greater than Class C. Both Class A and B pertain to isotopes that have relatively short half-lives which should be completely decayed within 500 years. Class C pertains to radioactive species that have long-lived isotopes which cause them to be potential environmental hazards into the remote future. The upper activity limits allowed in the Class C category vary with each isotope. For example, the activity limit for ^{14}C in activated metal waste is 80 Ci/m^3 . Greater than Class C pertains to waste that exceeds the allowed Class C limits.

There are a number of isotopes that meet the criteria required of a Class C waste material and ^{14}C is one of them. It has a half-life of 5730 years and decays by beta emission (E_{max} = 156 KeV) to the stable ^{14}N isotope. ^{14}C is found in nuclear hardware and is an activation product formed by the interaction of thermal neutrons with ^{14}N [$^{14}N(n,p)^{14}C$].

There are three major obstacles which cause this analysis to be difficult. First, it is difficult to analyze beta emitting isotopes due to their non-discreet decay energies. Therefore, chemical separations to remove radioactive species that have interfering decay energies, i.e., other beta or alpha emitting isotopes, is required prior to scintillation counting (3). This process can be complicated and time consuming. Second, the highly radioactive state of many of the samples imposes the need to perform the separation in a remote, shielded facility. This is not only time consuming but also physically taxing on the analyst. Third, the ^{14}C is often trapped in sample with matrices that are very difficult to work with. For instance, for chemical separations, a sample must be completely dissolved to ensure homogeneity. Incomplete dissolution could result in quantitative error in the results. These three major obstacles are bypassed by using the modified remotized LECO® carbon analyzer which is described in this paper.

EXPERIMENTAL

General Description

The Analytical Laboratory routinely measures total carbon content of radioactive samples using a LECO® HF-400/IR-412 carbon analyzer that has been modified to operate in the ALHC. For an analysis, the solid sample is placed in a ceramic crucible along with a granulated metal called an accelerator. The accelerator provides coupling between the sample and an induced high radio-frequency (RF) magnetic field. This, in turn, produces sufficient induction heating to combust the sample that is purged using a stream of pure oxygen. The crucible is placed in the instrument's induction furnace. Upon combustion, all of the carbon within the solid matrix of the sample is released in the form of CO and CO_2. The CO is quantitatively converted to CO_2 by passing the gaseous products through a hot rare earth copper oxide (350E C) reagent tube.

In the traditional mode of operation, the CO_2 product was analyzed by IR adsorption for total carbon. The CO_2 would then be exhausted back into the ALHC. However, the need to analyze specifically for ^{14}C required that the system be modified. A removable solid sorbent CO_2 trap was fabricated and inserted in the remote furnace carbon analyzer exhaust piping and is shown in Figure 1. The system was reconfigured so that all of the CO_2 product would be selectively adsorbed onto carbon molecular sieve within the trap. This trap could then be detached from the exhaust piping and purged with nitrogen, N_2, to remove all of the adsorbed CO_2. The entrained CO_2 would subsequently be bubbled through an amine solution to complex CO_2. The schematic diagram of this system is shown in Figure 2. Having successfully separated ^{14}C as $^{14}CO_2$ from the other beta emitters in the wasteform, a known quantity of the amine/CO_2 complex was mixed with a compatible liquid scintillation cocktail and quantitatively counted for ^{14}C beta activity.

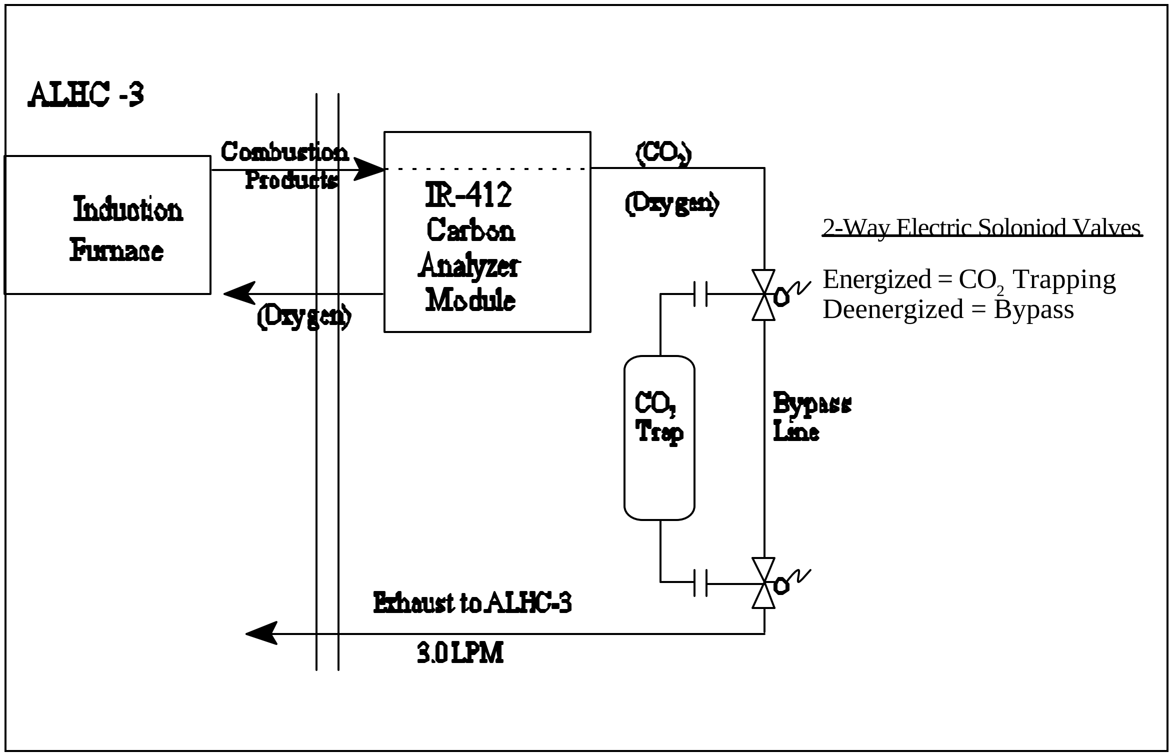

Fig. 1. Carbon Dioxide Trap.

Solid Sorbent Carbon Dioxide Trap

A solid CO_2 adsorbing material had to be found for the trap which would be placed in the exhaust piping (Figure 1). Different solid sorbent trapping agents were tested for this purpose. There were specific requirements for this material that were governed by the operating parameters of the analyzer. These requirements included that the adsorbent must have complete retention of CO_2 during the combustion process (60-90 seconds) at a 3.0 L min^{-1} oxygen flowrate at room temperature under a minimum back pressure of <0.25 psi.

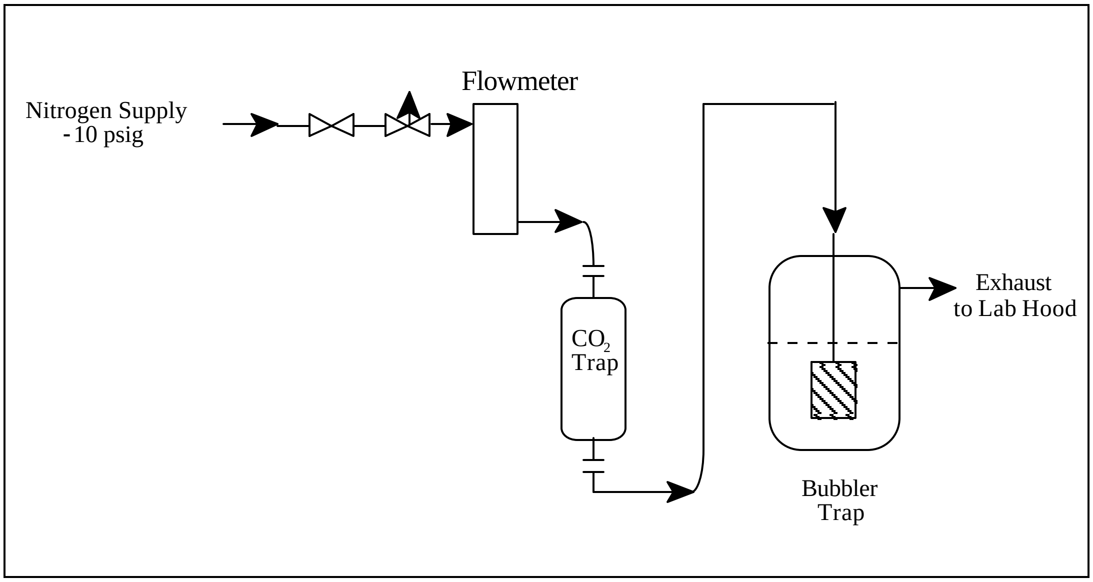

Fig. 2. Carbon Dioxide Removal/Capture in Laboratory Hood.

Alltech CARBOSPHERE® carbon molecular sieve (60/80 Mesh) adsorbent was found to possess the qualities needed for complete adsorption of CO_2. Forty grams of the CARBOSPHERE® completely retained CO_2 up to 160 seconds at 25E C using the above mentioned oxygen flowrate of 3.0 L min^{-1}. This maximum retention time was well over the 60-90 second range that would actually be needed for sample combustion.

^{14}C Stainless Steel Standard Preparation

A trial series of tests were performed on a set of twelve stainless steel ^{14}C standards. These standards were prepared using a NIST traceable standard (# 493-12-2). These tests were performed to confirm the capabilities of the modified LECO® analyzer.

Twelve stainless steel discs that were 0.75" in diameter with masses of 1.2 g were obtained. A 0.10-mL volume of the ^{14}C NIST standard solution was deposited on each of the discs. The discs were allowed to air dry overnight in a laboratory hood. The ^{14}C activity deposited on each of the discs was 22,600 dpm which had been verified by liquid scintillation counting. To verify the stability of the NIST standard, a prepared ^{14}C stainless steel standard was acid washed to remove deposited ^{14}C activity and counted. The results showed that they were in acceptable agreement.

Accelerator/^{14}C Stainless Steel Standard Combustion Test

The correct choice of accelerator was imperative in order to achieve a complete melt of the sample. Three accelerators were tested for optimal performance. These included, high purity granular iron, high purity granular copper, and a trademark accelerator, LECOCEL® II HP, which is a mixture of 22 mesh tin and tungsten. The LECOCEL® accelerator is normally used for lower temperature melts. The use of this alone did not provide sufficient inductive coupling to reach the high temperature needed to completely melt the stainless steel samples. Various combinations of the three accelerators were tried. When pure iron accelerator was used, which is a high temperature accelerator, a ceramic crucible cover (with a venting hole in the middle) was placed on the crucible. The reason being is that the excessive splatter from using the iron can damage the glass combustion tube into which the crucible is placed. Higher temperature melts generally require the use of crucible covers because of splatter. It was found that a mixture of approximately 1 gram each of the iron and LECOCEL® accelerator provided the optimal coupling for a complete melt of the stainless steel samples resulting in a RF plate current reading between 425-450 mA.

There is a time delay between the onset of combustion when CO_2 forms and when the gas reaches the IR detector. Without crucible covers that delay time is 15 seconds after the onset of combustion and the detector response normally extends out to 45 seconds before the CO_2 curve decays down to the baseline. However, with the use of crucible covers in this higher temperature experiment, the delay response was 18 seconds and the detector response extended out to about 60 seconds. This extended response time was sufficient for quantitative trapping of CO_2 on the carbon molecular sieve.

Parameters for CO_2 Product Treatment

The combustion of the stainless steel ^{14}C standards as described above was accomplished when the CO_2 product was completely adsorbed on the carbon molecular sieve in the trap located in the exhaust piping outside of the hot cell. The objective at this time was to quantitatively release the trapped CO_2 from the molecular sieve into a medium that would react completely with the released CO_2 to form a stable compound which would, in turn, be compatible with the selected liquid scintillation cocktail to be used for beta detection.

CO_2 Purge Medium The CO_2, when purged from the the molecular sieve trap, must be collected in some liquid medium for liquid scintillation counting. There were two requirements which would determine the choice of this liquid. First, it was essential that it retain the CO_2 in some stable form, and second, it must be compatible with the 'cocktail' used during ^{14}C liquid scintillation counting (LSC). A commercial organic amine called CARBOSORB® E was chosen. The proposed mechanism suggests that CO_2 reacts with the amine in the CARBOSORB® to form an unstable intermediary nitrogen substituted carbamic acid. The general equation goes as follows:

$$\mathrm{RNH_2 + CO_2} \;\; \mathbf{v} \;\; \mathrm{RNHCOOH} \qquad \text{(Eq. 1)}$$

Nucleophilic substitution of another amine molecule on the carbamic acid then gives a stable disubstituted urea and water

$$\mathrm{RNH_2 + RNHCOOH} \;\; \mathbf{v} \;\; \mathrm{RNHCONHR + H_2O} \qquad \text{(Eq. 2)}$$

Essentially, the CO_2 gas has been converted to a stable urea homologue(4,5).

Purge gas Nitrogen was found to be an effective purge gas for the removal of CO_2 from the molecular sieve trap. To test its effectiveness, the nitrogen was bubbled through the CARBOSORB® which was periodically removed and counted for ^{14}C activity. After each removal of the used CARBOSORB®, fresh medium was poured into the bubbler and nitrogen purging was continued. The results of the test are shown in Table I. In less than four hours of purging the trap with nitrogen, 91% (20,561 dpm) of the total ^{14}C activity (22,600 dpm) had been removed from the molecular sieve. Additional purging showed that after 16 hours, 92% of the ^{14}C had been removed. Two additional hours of purging showed no ^{14}C removal. The optimal time then, for purging with nitrogen, appeared to be 4 hours.

Table I. CO_2 Recovery from The Molecular Sieve Trap using A Nitrogen Purge

Purge Time	^{14}C Activity Recovered	Additive ^{14}C Recovery
0-60 min	6677 dpm	6677 dpm
60-120 min	12651 dpm	19328 dpm
120-240 min	1233 dpm	20561 dpm
Overnight (+16 hrs)	255 dpm	20816 dpm
+ 2 hr	no additional activity	no additional activity

Liquid Scintillation Counting(LSC)

The ^{14}C activity was counted with the Packard 2500TR Liquid Scintillation Analyzer. The scintillator or 'cocktail' chosen was PERMAFLUOR® E+. The 30 mL of the CO_2/amine product was brought up to 60 mL with additional PERMAFLUOR®. Three milliliters of this solution was then combined with 17 mL of the LSC cocktail in a scintillation vial. The energy window used for the ^{14}C scintillation counting was 0-156 KeV. This energy range was chosen because the beta particles emitted from the ^{14}C isotope is within these energy boundaries with a maximum of 156 KeV.

The general experimental conditions found to be essential for efficient separation of carbon from the stainless steel standards in the form of CO_2 are listed in Table II.

Table II. Experimental Parameters for CO_2 Separation from Stainless Steel Samples

Accelerators	~ 1 g each iron and LECOCEL®II
Sample Type	1.2 g stainless steel disc (^{14}C=22600dpm)
Combustion Time	0-75 sec
CO_2 Trapping Time	0-75 sec
Purge Gas	Nitrogen
Purge Flowrate	175 cc/min
Trap Heating	70E C
Purge Time	4 hr
Amine Volume	30 mL

RESULTS

^{14}C Stainless Steel Standards

To validate the method described above, four additional ^{14}C stainless steel standards were taken through the experiment. Table III lists the results of this ^{14}C standard assay.

Table III. Results of ^{14}C Standard Assay

Standard ID #	Recovered ^{14}C Activity (DPM)*	% Recovery
1	23,028	102
2	22,374	98.8
3	21,057	93.0
4	22,341	98.7

* Standard ^{14}C activity = 22,600 DPM

These results showed quantitative recovery of the ^{14}C activity. The average ^{14}C acivity and recovery for this data set is 22,200 DPM and 98.2 % respectively.

Sensitivity of The Liquid Scintillation Counting (LSC)

The limit for ^{14}C activity in activated metal is 80 Ci/m^3 for Class C Waste requirements.(1) This activity for stainless steel would be equivalent to 10 µCi/g which is easily detected by liquid scintillation counting. The minimum quantifiable level (MQL) used for this methodology is based on a nominal one gram sample, a LSC background of 35 dpm, and direct counting of a 20-mL aliquot from the 60 mL CARBOSORB®/PERMAFLUOR® solution. The MQL was chosen empirically and a signal that is twice that of background was found to be a conservative estimate. Using the above conditions, the MQL has been calculated as follows,

$$(35\ \text{dpm}/1.0\ \text{g})(1\ \mu\text{Ci}/2.22\ \text{E}\ 6\ \text{dpm})(60\ \text{mL}/20\ \text{mL}) = 4.7\ \text{E}\ {-5}\ \mu\text{Ci/g} \qquad \text{(Eq. 3)}$$

Determination of ^{14}C in Cladding Hull Samples

The verification that quantitative recovery was possible by using this methodology allowed for its application to actual samples. The first samples obtained for this purpose, were irradiated stainless steel cladding hulls that had been cut into small sections. Cladding hulls are essentially reactor hardware used to contain the fuel elements and a waste product from reprocessing spent fuel. The results of total carbon and radiocarbon (^{14}C) for five cladding hulls are shown in Table IV.

Table IV. ^{14}C Analysis of Cladding Hulls.

Sample ID	Sample Wt.(g)	Total Carbon (µg/g)	^{14}C Activity (µCi/g)
CH#1	0.6105	506	0.14
CH#2	0.5996	504	0.12
CH#3	0.6041	569	0.19
CH#4	0.6059	539	0.17
CH#5	0.5971	490	0.17

The beta spectra of each sample was examined for any apparent activity due to contaminants. The spectra showed that the separation of ^{14}C activity from other radioisotopes present in the cladding hulls had been successful.

^{14}C Assay of Irradiated Beryllium Metal

Twelve irradiated beryllium metal samples from the Advanced Test Reactor (ATR) were received for ^{14}C analysis. Beryllium metal is hardware used as neutron reflectors blocks in some nuclear reactors. The samples were cut into small pieces and weighed prior to analysis. Table V shows the results of total carbon and radiocarbon (^{14}C) for these samples.

Table V. Beryllium ^{14}C Results

Sample ID	Total Carbon (µg/g)	^{14}C Activity (µCi/g)
79778	734	0.61
79779	637	0.24
79780	824	0.58
79781	804	0.35
79782	693	0.18
79783	681	0.41
79784	650	0.36
79785	1100	0.52
79786	678	0.51
79787	715	0.29
79788	665	0.33
79789	761	0.35

Variance of ^{14}C Activity between Standards and Actual Samples

The ^{14}C activity measured in the cladding hull samples or the beryllium samples exhibited higher variance (Tables IV & V) when compared to the ^{14}C stainless steel standards. This is due to two factors. First, the distribution of ^{14}N (the precursor to ^{14}C) within the material from which the samples were taken, is not necessarily homogeneous. Second, the location each sample in the reactor is unique. Each one will be exposed to different levels of neutron irradiation required for the $^{14}N(n,p)^{14}C$ reaction. Due to the variability within the cladding hull and beryllium data sets, the precision and accuracy of the method was proven by performing the process with the stainless steel standards. Based on this data, the 2-sigma precision of this method is ± 7.4 %.

CONCLUSION

Prior to the modified system which combined remote high temperature combustion followed by CO_2 trapping, followed by liquid scintillation counting for ^{14}C beta activity, there was no available commercial methodology for quantifying ^{14}C in activated metal waste. The obstacles of ^{14}C analysis in activated metal waste have been surmounted by using this technique. It offers a convenient approach for extracting ^{14}C from a sample contaminated with other radioisotopes which would otherwise interfere with ^{14}C characterization. Quantitative yield of ^{14}C was obtained from stainless steel standards which proved the accuracy of this method. Sample throughput is constrained by the four hour purge time required for the quantitative removal of CO_2 from the carbon molecular sieve trap. However, faster removal of CO_2 could be attained by increasing the temperature of the trap while purging with nitrogen.

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