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CONF-800427--22

**DIFFERENTIAL MONITORING OF TRITIUM AND
CARBON-14 COMPOUNDS****R. W. Goles
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the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830.****Pacific Northwest Laboratory
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INTRODUCTION

Of the radioactive elements which can be expected to be released to the environment during nuclear related operations, ^3H and ^{14}C are among the most important from a radiological health standpoint (Dr65; Bu74). Both ^3H and ^{14}C are capable of forming numerous, chemically different, volatile molecular species some of which are extremely difficult to control on an industrial scale. Moreover, the chemical forms assumed by these isotopes as they enter and pass through the environment are of fundamental radiological importance since their chemistry will determine mobilities, atmospheric residence times, long term environmental effects and the biological significance of these isotopes. Consequently, any investigation designed to characterize ^3H and ^{14}C emissions has to address itself to the many chemical identities assumed by these isotopes.

Differential sampling for selected chemical species of both ^3H and ^{14}C has been reported in the literature (Os74; Mi76; Th78). However, these investigations have had limited scopes and have employed sampling techniques that cannot be combined readily to form a fully integrated ^3H - ^{14}C species-selective sampling system. Consequently, a gaseous sampling system was developed to differentially collect all major volatile forms of tritium and carbon-14 according to chemical class. These chemical forms include: tritiated forms of water, hydrogen and organics; as well as ^{14}C -containing carbon monoxide, carbon dioxide and organics. Sampling campaigns involving the use of this differential ^3H and ^{14}C collection system have been successfully conducted at a high level liquid waste solidification plant, at a spent fuel storage facility and in the vicinity of power reactors.

SAMPLING SYSTEM

The chemically specific sampling system developed to differentially collect all major volatile forms of ^3H and ^{14}C is illustrated in Fig. 1. The underlying basis of this differential sampling system is that of controlled oxidation. By employing various catalysts and trapping agents in the proper order, one can selectively remove each of the previously mentioned chemical compounds from a sampling air stream in a sequential manner. This is accomplished by initially desiccating the sampled air to remove all isotopic forms of water. The dried air then passes through a caustic bed that removes all forms of carbon dioxide. A room temperature Pd catalyst is subsequently employed to oxidize the hydrogen component of the air stream, and a desiccant immediately collects the oxidation product. The sampled air next passes through a mixed oxide, room temperature catalyst, *Hopcalite*[®], that oxidizes carbon monoxide. The catalytically formed CO_2 is then collected by a caustic trapping agent. Finally, all organic constituents are combusted with a 600°C Pt converter and the oxidation products, water and carbon dioxide, are removed as previously, described. Molecular sieve material with an effective pore size of 3A[°] was used as the primary dessicating material in these studies while the commercially available product *Ascarite*[®] was used to collect carbon dioxide. To insure quantitative removal of the sought after chemical compounds, a carrier gas containing stable isotopic forms of H_2 , CO and CH_4 was bled into the sampled gas stream prior to any

[®]*Hopcalite* is a registered trade mark of MSA - Mine Safety Appliance Company, Pittsburgh, PA.

[®]*Ascarite* is a registered trade mark of the Arthur H. Thomas Company, Philadelphia, PA.

contact with chemically specific traps.

Chemical specificity of the various catalysts employed in this sampling system were investigated whenever appropriate. Catalytic activity was determined through use of a series of alternating catalysts and absolute chemical traps. Catalytic efficiencies were determined gravimetrically by extracting and weighing the oxidation products, water or carbon dioxide, present in successive traps according to the relation:

$$\epsilon = 1 - W_2/W_1$$

where ϵ is the collection efficiency per stage and W_1 and W_2 are the quantities of trapped material in successive stages. The collection efficiency associated with chemically specific trapping materials were similarly determined but without the use of catalytic agents. The results of these studies are summarized in Tables I and II.

SAMPLE PROCESSING AND ANALYSIS

^3H

The three sampled forms of tritium—tritiated water, hydrogen and organics—were all collected in the chemical form of water on a molecular sieve desiccant. The water was extracted from this desiccant by vacuum distillation at 560°C. In the case of the hydrogen and organic tritium traps, where the quantity of collected water is small, "dead water" was used to push out the sample memory left on the desiccant (Os70). This method allows the total sample to be extracted from the desiccating material.

After extraction of the water samples, aliquots were taken and mixed with a liquid scintillator, *Insta-Gel*,[®] and counted with liquid scintillation

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counter. For overnight counts, the sensitivity of this analytical system was such as to yield a minimum detectable (Cu68) tritium concentration of 1 pCi/m^3 .

^{14}C

All forms of sampled ^{14}C , carbon dioxide, carbon monoxide, and organics were collected in the chemical form of CO_2 , on a caustic bed of *Ascarite*. Chemically *Ascarite* is NaOH suspended on an asbestos substrate. The collected CO_2 sample was extracted by dissolving it in water and precipitating the resultant $\text{CO}_3^{=}$ ion with Ba^{++} .

The extracted samples of ^{14}C were then analyzed using liquid scintillation techniques. In this method, (Ha77) a liquid scintillation compatible CO_2 absorber, *Carbo-Sorb*[®] (basic amine), was utilized in a bubbler that formed part of a closed-loop recirculation system. The sample, in the form of BaCO_3 , was introduced into the closed system and acidified to convert the sample to CO_2 . The CO_2 was continuously recycled through the *Carbo-Sorb*[®] until absorption was complete. The absorbed sample was then mixed with a toluene-based scintillator, *Permafluor II*,[®] and counted with a liquid scintillation detection system. The minimum carbon-14 detection limit (Cu68) associated with this analytical system is nominally 0.5 pCi/m^3 for 1000 min counting intervals.

SAMPLING RESULTS

Sampling campaigns involving the use of the differential $^3\text{H} - ^{14}\text{C}$ collection system described above have been conducted at a nuclear waste solidification plant, at a spent nuclear fuel storage facility and in the

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vicinity of nuclear power reactors. The results obtained from each of these studies will now be individually discussed.

NWVP

The Nuclear Waste Vitrification Project (NWVP) was initiated to demonstrate the vitrification of high-level liquid waste (HLLW) generated from spent power reactor fuel. This involved the dissolution of spent (8-year cooled) enriched uranium fuel, the separation of uranium and plutonium isotopes from the dissolver solution and finally the vitrification of all unextracted fission product activity present in the liquid waste stream. In all, the equivalent of 2 MTU was reprocessed during a four month long campaign. Throughout this entire period, process related emissions of tritiated forms of water and hydrogen were characterized on an averaged weekly basis. This data appears in Fig. 1. In addition, specific emissions associated with the dissolution and vitrification steps of the reprocessing cycle were selectively examined with regard to ^3H and ^{14}C . This data appears in Table III. Clearly the major gaseous chemical forms of tritium and carbon-14 that successfully escaped the NWVP process were water and carbon dioxide, respectively. This was true not only for the entire process as a whole but was also the case during the discrete steps of dissolution and vitrification.

Morris Facility

Chemically specific sampling for both tritium and carbon-14 has been conducted at the General Electric spent fuel repository located at Morris, Illinois. Although originally designed as a fuel reprocessing facility, the Morris plant has never gone hot; consequently, no uncertainty with regard to source terms exists within the plant itself. However, because the

Dresden power reactor station lies in close proximity to the Morris plant, two differential ^3H - ^{14}C samplers were employed in this study—one sampling the plant's inlet air plenum and the other sampling the fuel storage basin exhaust. The results obtained from this sampling campaign are summarized in Table IV. Like the off gas emission associated with NWVP, the major gaseous chemical forms of tritium and carbon-14 emanating from the storage basin are water and carbon dioxide, respectively. The specific activity of storage basin water as routinely determined by plant personnel compares quite favorably with the value derived from the study as is seen in Table IV. No plant data exists for the ^{14}C contained in storage basin water.

Power Reactors

Differential ^3H and ^{14}C sampling has been conducted in the vicinity of two different types of power reactors—Hanford's N-Reactor and General Electric's Dresden facility. N-Reactor is a dual purpose power and plutonium production reactor while the Dresden station is a more or less conventional LWR power reactor. Direct stack gas sampling was not possible at either facility. Consequently, environmental air sampling around reactor sites were conducted. Sampling at these two sites differed only in that carbon-14 was not collected at the N-Reactor site. As might be expected, no significant ^3H or ^{14}C reactor related emission were detected.

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Table IV - Spent Fuel Storage Facility Emissions.

TABLE I. EXPERIMENTAL CATALYTIC OXIDATION EFFICIENCIES

<u>Catalyst</u>	<u>Reactant</u> *	<u>Temperature</u> <u>°C</u>	<u>Product</u> <u>Sampled</u>	<u>Conversion</u> <u>Efficiency</u> <u>%</u>
Palladium	CO	20	CO ₂	15 ± 5
Palladium	CH ₄	20	H ₂ O	< 1
<i>Hopcalite</i> ®	CO	20	CO ₂	>98
<i>Hopcalite</i> ®	CH ₄	20	H ₂ O	< 1
Platinum	CH ₄	600	H ₂ O	>99

* Molecular concentration in air ~0.2%

TABLE II. SAMPLING PARAMETERS ASSOCIATED WITH CATALYSTS AND TRAPPING AGENTS

<u>Material</u>	<u>Function</u>	<u>Residence Time (sec)</u>	<u>Loading Capacity (Wt%)</u>
Zeolite	Desiccant	.05 ^(a)	10 ^(a)
Ascarite [®]	CO ₂ Trap	.5	4
Pd	Catalyst	.05 ^(a)	---
Hopacalite [®]	Catalyst	.6 ^(b)	---
Pt	Catalyst	1.0 ^(b)	---

(a) From Reference Os74.

(b) Minimum values have not been determined.

TABLE III. NWVP STACK EMISSIONS

<u>Isotope</u>	<u>Chemical Form</u>	<u>Concentration (pCi/m³)/(% Error)</u>		
		<u>Pre NWVP</u>	<u>Dissolution</u>	<u>Vitrification</u>
³ H	Water	80/(5)	41,000/(5)	1,000/(5)
	Hydrogen	6/(10)	36/(5)	20/(20)
	Organics	30/(5)	160/(5)	15/(15)
¹⁴ C	Carbon Dioxide	3/(10)	814/(5)	110/(5)
	Carbon Monoxide	Bkg/(10)	20/(5)	20/(5)
	Organics	Bkg/(10)	Bkg/(10)	23/(5)

TABLE IV: SPENT FUEL STORAGE FACILITY EMISSIONS

<u>Isotope</u>	<u>Chemical Form</u>	<u>Concentration (pCi/m³)</u>	<u>Error (%)</u>
³ H	Water	1,700	5
	Hydrogen	Bkg	20
	Organics	Bkg	20
¹⁴ C	Carbon Dioxide	300	5
	Carbon Monoxide	Bkg	10
	Organics	Bkg	10

LIST OF FIGURES

Fig. 1 Schematic of ^3H - ^{14}C Sampling System.

Fig. 2 NWVP Weekly Averaged Tritium Emissions.