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Mass Spectrometric Determination of
 $^{18}\text{O}/^{16}\text{O}$ Ratios to Locate the Source of
Oxygen in Snap Fuel Capsule Components

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MASS SPECTROMETRIC DETERMINATION OF $^{18}\text{O}/^{16}\text{O}$ RATIOS TO LOCATE THE SOURCE OF OXYGEN IN SNAP FUEL CAPSULE COMPONENTS

by

M. E. Smith and G. R. Waterbury

ABSTRACT

The successful application of a mass spectrometric method to determine the source of oxygen diffusion into the container material of a radioisotopic fuel capsule is described. The source was chiefly the oxide fuel ($^{238}\text{PuO}_2$) and not the atmosphere. The radiochemical method, based on an α -n reaction, could not be applied because of the very low α -particle flux in the liner material.

INTRODUCTION

Embrittlement and resultant loss of physical strength of the tantalum alloys used as container material for fuel capsules for radioisotopic generators required the measurement of oxygen as well as other interstitials in trace quantities. The inert gas fusion method used at the Los Alamos Scientific Laboratory proved satisfactory for measuring the oxygen, and the results showed that the embrittlement was caused by high oxygen contents. Therefore, we had to determine whether the source of the oxygen contamination was from the fuel or from the atmosphere so that a more suitable container could be designed. This could be accomplished by determining the $^{18}\text{O}/^{16}\text{O}$ ratio in the tantalum alloy material, because the ^{18}O content of the fuel had been reduced to minimize α -n reactions. The $^{18}\text{O}/^{16}\text{O}$ ratio was $\sim 5.5 \times 10^{-4}$ for fuel as compared with 2×10^{-3} for air. A radiochemical procedure based on the reaction $^{18}\text{O}_8 + {}^4\text{He}_2 = {}^{21}\text{Ne}_{10} + {}^1\text{n}_0$, used successfully in determining ^{18}O in $^{238}\text{PuO}_2$, could not be applied because of the very low α -particle flux within the tantalum samples. However, we were able to adapt an existing mass spectrometric method used originally to determine $^{18}\text{O}/^{16}\text{O}$ atom ratios in plutonium oxide.¹ With this method, we established that the source of the oxygen was chiefly the oxide fuel.

APPARATUS AND REAGENTS

The apparatus includes an inductively heated platinum bath in a graphite crucible for reacting the sample with carbon to form carbon monoxide, a silica gel trap cooled in liquid nitrogen, a preparative gas chromatograph for separating carbon monoxide and nitrogen, and a mass spectrometer for measuring the $^{12}\text{C}^{18}\text{O}/^{12}\text{C}^{16}\text{O}$ ratio. The apparatus and reagents used are described in detail in Ref. 1. The carbon content of the platinum bath is adequate for the formation of sufficient carbon monoxide; therefore, the addition of graphite powder is not necessary. This eliminates the need for a mixing capsule, pellet press, etc., used with the oxide samples.¹

SAMPLE PREPARATION

The metal samples were degreased with Freon and the surface abraded with a clean file. Samples containing less than ~ 500 ppm oxygen were considered inadequate for analysis. Those samples suspected of containing too little oxygen were analyzed first for total oxygen using an inert gas fusion procedure.²

RECOMMENDED PROCEDURE

The recommended procedure¹ involves inductively heating the samples with platinum contained in a graphite crucible to ~2000°C, sweeping the generated carbon monoxide with helium through a trap containing silica gel cooled with liquid nitrogen, and desorbing the gases from the trap into a preparative gas chromatograph to separate the nitrogen and collect the carbon monoxide. The carbon monoxide obtained is analyzed with a mass spectrometer to measure the $^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{16}\text{O}$ peak heights to calculate the $^{18}\text{O}/^{16}\text{O}$ ratio. The detailed step-wise procedure is described in Ref. 1.

EXPERIMENTAL

A typical example indicating diffusion of oxygen into the liner (Ta-10W) from the plutonium fuel, which had an $^{18}\text{O}/^{16}\text{O}$ ratio of about 5.5×10^{-4} , is shown in Table I. Diffusion of oxygen from the atmosphere would have resulted in ratios of 2×10^{-3} . Analysis of the strength member T-111 (Ta-8W-2Hf) samples showed diffusion of oxygen from the fuel with the ranges presumably resulting from nonuniform contact with the liner. An example of this is shown in Table II.

Table III, from the work of Mulford and Bronisz,³ shows the oxygen content of the components from three capsules. The embrittlement of the components caused by the oxygen is described in their report.

CONCLUSION

Careful application of this mass spectrometric method resulted in conclusive proof of the source of oxygen in the capsule components, an achievement not possible by any other known method.

TABLE I

RATIOS OF $^{18}\text{O}/^{16}\text{O}$ DETERMINED IN A Ta-10W LINER OF A SNAP FUEL CAPSULE

$^{18}\text{O}/^{16}\text{O}$ Ratio ^a	Total Oxygen (ppm)
4.6×10^{-4}	2000
4.7×10^{-4}	1400
4.9×10^{-4}	2000
7.9×10^{-4}	1000

^aSamples taken from different locations on the liner.

TABLE II

RATIOS OF $^{18}\text{O}/^{16}\text{O}$ DETERMINED IN A SNAP CAPSULE STRENGTH MEMBER

$^{18}\text{O}/^{16}\text{O}$ Ratio	Location
6.8×10^{-4}	Body
5.8×10^{-4}	Body
5.6×10^{-4}	Dome near pressure release orifice
6.9×10^{-4}	Weld zone
5.9×10^{-4}	Weld zone

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TABLE III

HEAT SOURCE CAPSULE HISTORIES

Capsule	Time (days)	Temp (°C)	Oxygen Content, ppm	
			Liner	Strength Member
PF-1 (Pioneer)	210	825-850	1300-3700 (85%) ^b	500-1900 (85%)
PF-3 (Pioneer)	175	825-850	1000-2000 (85%)	400- 600 (100%)
TF-1 (Transit)	226	650-700 ^a	900-1600 (60%)	175- 235 (7%)

^aOne day at 825°C.

^bNumbers in parentheses indicate the amount of oxygen that came from the fuel.

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