

DETERMINATION OF TRACE IMPURITIES IN ZIRCALOY-2 AND TELLURIUM BY SPARK SOURCE MASS SPECTROMETRY

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Determination of trace impurities in zircaloy-2 and tellurium by Spark Source Mass Spectrometry (SSMS) is reported. The advantage of SSMS lies in the fact that along with metallic trace constituents even the nonmetallic impurities and gases including hydrogen can also be determined.

Introduction

Purity control and the detection of a number of trace elements present in some of the important materials finding applications in semiconductor and nuclear technologies is an important type of analytical task. Zircaloy-2, for example, is employed in nuclear industry as cladding material and consequently its purity against the presence of high thermal neutron absorbing materials should be guaranteed. Similarly, the presence of excess of hydrogen over a certain specification limit may eventually lead to its brittleness under the severe conditions of reactor operation. Tellurium is employed in semiconductor industry for the preparation of mercuric cadmium telluride used in infrared detectors. It is a great advantage if it is possible to determine all the elements present in the samples in the course of a single analysis by means of a single analytical method. The versatile characteristics of Spark Source Mass Spectrometry (SSMS) such as high sensitivity, uniform selectivity and the simultaneous multielement analysis capability, makes it an attractive technique of choice for obtaining a panoramic analysis. The advantage of SSMS is that detection limits of 0.1 ppm are obtainable for almost all elements including those elements such as C, N, O, F, P which are difficult to detect by means of other multielemental analysis procedures. Further, hydrogen can be determined by adopting a two level exposure technique.¹ In our laboratory SSMS is being employed for the analysis of materials having relevance in nuclear technology. This paper gives the details of such application for the analysis of zircaloy-2 and tellurium and discusses the results obtained.

Experimental

Instrument

The instrument employed in the present work is a JMS 01BM-2 Mattauch Herzog double focusing rf-spark source mass spectrometer with a spherical electrostatic analyzer and an auto spark controlling unit. The spherical electrostatic analyzer helps in the focusing of the ion beam in Z-direction. The auto spark controller adjusts the position of one of the electrodes inside the ion source during sparking so as to keep the sparking position fixed. This is useful when long exposures are taken on the photoplate. The instrument has 4 polyphenyl ether oil diffusion pumps and one getter ion pump which routinely give a pressure of less than $1 \cdot 10^{-7}$ and $1 \cdot 10^{-8}$ Torr in ion source and the analyzer, respectively. The oil diffusion pumps are provided with liquid nitrogen traps to retain the adsorbed gases such as moisture. Further details of the instrument operation have been given elsewhere.^{2,3}

Samples and sparking conditions

Zircaloy-2: An end plug of zircaloy clad was machined into cylindrical electrodes (10 mm \times 2 mm). They were cleaned with concentrated hydrochloric acid, washed thoroughly with doubly quartz distilled water and subjected to ultrasonics in acetone. They were vacuum dried and immediately taken for analysis. The sparking conditions employed were: power amplifier anode voltage = 3 kV; acceleration voltage = 30 kV; pulse repetition frequency = 3 kHz; pulse width = 40 μ s; electrostatic voltage = 3 kV; main slit = 50 μ m; and α , β slit widths = 0.8 mm each.

Tellurium: Semiconductor grade tellurium flakes were melted in quartz ampoules to get cylindrical electrodes. These electrodes were treated in the same way as zircaloy-2 electrodes before taking up for sparking. Except for the pulse width (20 μ sec) and pulse repetition frequency (1 kHz) all the other sparking conditions were maintained same as for zircaloy-2 sparking.

The electrodes were presparked to about 1×10^{-8} C. Ilford Q-2 photoplates (350 mm \times 50 mm \times 1 mm) were employed as photoplate detector. The exposures on the photoplate were taken in the decreasing order from $3 \cdot 10^{-7}$ C to $1 \cdot 10^{-13}$ C so as to keep the sparking area free from the readsorbed gases.

Determination of hydrogen

A two level exposure technique described earlier¹ has been employed for determining hydrogen in zircaloy-2. The photoplate was exposed at two different sets of magnetic fields (14000 G and 4000 G for example) so as to cover the entire mass

range from H to U. The concentration of hydrogen was determined with respect to an intermediate reference element which could be determined with respect to the matrix element directly. The instrument was operated at a practical resolution of about 2000. During the experiment the pressure in the ion source was $1 \cdot 10^{-7}$ Torr and in the analyser $5 \cdot 10^{-8}$ Torr.

Results and discussion

Table 1 gives the concentration of the trace elements determined in the two matrices investigated. The concentrations are given with respect to the corresponding matrix element zirconium and tellurium. It should be mentioned that the figures indicated are the observed concentrations and no calibration factors such as relative sensitivity coefficients (RSCs) have been applied. The concentration of the trace elements have been determined after carefully considering the interfering mass numbers in each of the samples. In cases wherever possible, more than one isotope of the element was monitored to calculate the concentration.

Zircaloy-2: Examination of the mass spectrum recorded on the photoplate revealed that only Zr forms oxide to a significant extent. Only doubly charged peaks of Zr could be predominantly seen as compared to those of ZrO. The multiply charged ions of tin, another major element ($\sim 2\%$) present extend up to the +4 state. The major interferences can therefore be expected at iron mass region. While the non-interference at mass number 55 (Mn) due to $^{94}\text{ZrO}^{2+}$ was confirmed by the absence of a peak at mass number 53.5 due to $^{91}\text{ZrO}^{2+}$, the mass numbers at iron, 56 and 57 suffer from interferences due to $^{112}\text{Sn}^{2+}$ and $^{114}\text{Sn}^{2+}$, respectively, and therefore could not be determined.

Tellurium: Oxide peaks of Te could not be observed and also only doubly charged Te ions could predominantly be seen. Copper mass numbers could have interferences due to doubly charged tellurium ions $^{126}\text{Te}^{2+}$ and $^{130}\text{Te}^{2+}$ which are not resolvable.

It should be mentioned that for determining hydrogen in zircaloy-2 carbon has been employed as the intermediate reference element. As two sets of magnetic fields were employed in the two-level exposure technique, the effect of changing the magnetic field on the element was also studied by determining nitrogen concentration with respect to Zr as well as carbon in the two-level exposure technique. The values obtained were 56 and 58 ppm, respectively, which indicate that the ion beam composition does not get altered when the magnetic field is changed.

The concentration values obtained in the case of zircaloy-2 analysis in the present work, are compared with the specification limits for these trace elements in zircaloy-2 and also the certified values in SRM 360a zircaloy standard. These values are given

Table 1
Concentration of trace elements in Zircaloy-2 and tellurium

Element	Zircaloy-2			Tellurium value obtained, ppm
	Specification limit, ppm	Concentration determined, ppm	Certified value for NBS 360a, ppm	
Tin	1.7%	2.05%	1.42%	44
Iron	0.2%	NDD	0.144%	10.8
Chromium	0.15%	0.168%	0.106%	0.06
Nickel	800	941	554	1.1
Aluminium	75	159		2.4
Boron	0.5	0.12		0.19
Calcium	30	NDD		NDD
Carbon	270	225	136	0.12
Cobalt	20	NDD		NDD
Copper	50	104	140	NDD
Hafnium	200	ND		ND
Lead	130	4.4		31.5
Magnesium	20	98		2.88
Manganese	50	7.7	3	NDD
Niobium	100	7		ND
Silicon	120	NDD	51	11.8
Titanium	50	8	27	NDD
Hydrogen	25	6.8		0.05
Nitrogen	65	45	43	0.03
Oxygen	1400	NDD		NDD
Phosphorus		16.6		ND
Antimony		7.0		ND
Arsenic		13.4		ND
Fluorine		2.1		0.01
Chlorine		0.8		1.1
Bromine		ND		13.5
Iodine		ND		5.8
Selenium		ND		2.2

ND = Not detected.

NDD = Not determined due to interferences.

in Table 1. As can be seen, the values obtained in the present work agree within a factor of 2 with the specification limits and also with the NBS certified values for the standard SRM 360a. However, for quantification of the results investigations are being carried out to determine the Relative Sensitivity Coefficients (RSCs) for the trace elements in zircaloy-2 and tellurium trace constituent standards.

It should be mentioned that the value given for nitrogen in Te includes residual nitrogen in the ion source during sparking. It is however expected to be very small

(considering the vacuum in the ion source: better than $1 \cdot 10^{-7}$ Torr) when compared with the value shown in the table.

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