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James M. Hansel
E. A. Hakkila

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

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X-RAY SPECTROGRAPHIC DETERMINATION OF IRIDIUM IN LiH OR LiD

by

James M. Hansel and E. A. Hakkila

ABSTRACT

Iridium is determined in LiH or LiD using a fusion-x-ray fluorescence technique. Samples are fused at 870°K, the residue is dissolved in HCl, and the solutions are fumed with HNO_3 to remove chloride. Platinum is added as an internal standard, and the intensities of the $L\alpha_1$ x rays of iridium and platinum are measured. The Ir/Pt x-ray intensity ratio is compared to ratios measured for reference materials having known compositions which have been prepared in the same manner as the samples. The relative standard deviation for measuring 1 to 10 mg of iridium is between 2 and 0.4%. Thulium and lutetium interfere when present in amounts greater than approximately 1%.

I. INTRODUCTION

A method was required for determining iridium in concentrations up to 2% by weight in LiD and LiH with a precision approaching 1% relative. X-ray fluorescence was a promising technique for rapidly measuring iridium; however, the sample had to be prepared in a form suitable for analysis in the x-ray spectrograph. Pressing the lithium salt into pellets was considered first, but the hygroscopic nature of LiH or LiD and heterogeneous distribution of iridium in the pellets precluded this method of sample preparation.

Several acid dissolution techniques that used HNO_3, HCl, $HClO_4$, H_2SO_4, and various mixtures of these acids were used with only limited success. Dissolution could be attained with aqua regia after repeated decanting and boiling operations, but several hours of operator time was required.

A fusion-acid dissolution technique was satisfactory for dissolution of the samples, and a procedure based on this technique was developed for determining iridium in LiD and LiH. The dissolution method is rapid and eliminates acid leaching and high-pressure equipment normally required to dissolve iridium. One analyst can analyze approximately 15 samples per day.

II. APPARATUS

Balance, analytical, Ainsworth Model BCT, or similar.

Crucibles, nickel, 25-ml.

Furnace, muffle, Thermolyne, Type 1400, or similar.

Glovebox, inert atmosphere, having O_2 and H_2O concentrations of 2 ppm or lower.

Heat lamps, infrared, hard glass, with socket, switch, extension cord, and ring stand attachment.

Hot plate, Lindberg Hevi-Duty, or similar.

Mylar film, 6-μm thick.

Normal laboratory glassware, including beakers, pipets, volumetric flasks, etc.

Sample cells, polyethylene, Spex Industries, 25-mm-diam.

Tongs, metal.

X-ray spectrograph, vacuum, Philips Electronics, Inc., equipped with a LiF analyzing crystal, molybdenum-target x-ray tube, and scintillation detector with associated electronic counting circuitry, or equivalent spectrograph.

III. REAGENTS

Acid, hydrochloric, 12*M*, analytical reagent grade.

Acid, nitric, 16*M*, analytical reagent grade.

Iridium solution, dissolve enough iridium metal, using the hydrochloric acid bomb dissolution technique,[1,2] to provide a final solution containing 2.00 mg of iridium per milliliter.

Platinum solution, dissolve enough platinum metal in aqua regia to give a final solution containing approximately 2 mg of platinum per milliliter.

IV. X-RAY OPERATING CONDITIONS

X-ray tube, molybdenum-target, Philips FA 60.
Potential, 50-kV.
Current, 35-mA.
Counter, scintillation.
Analyzing crystal, LiF.
Count register, to accumulate 20 000 counts.

V. PROCEDURE

1. Accurately weigh 500-mg samples in an inert atmosphere glovebox, and transfer to 25-ml nickel crucibles.
2. Place the crucibles in a muffle furnace preheated to 873°K, and heat for 2 h.
3. Remove the crucibles from the furnace and allow to cool.
4. Cover each crucible with a watch glass, and carefully dissolve the fused sample in 12*M* HCl.
5. After the reactions have ceased, rinse the cover glass with distilled water, and transfer the dissolved sample to a 30-ml beaker.
6. Prepare, in 30-ml beakers, a series of known solutions containing the following amounts of iridium:
   a. 0 mg,
   b. 2.00 mg,
   c. 4.00 mg, and
   d. 10.00 mg.
7. Add 2.00 ml of the solution containing 2 mg of platinum per milliliter to each of the sample solutions and to each known solution.
8. Place each beaker on a hot plate heated to 363°K. Also heat the solution from above with infrared heat lamps, and evaporate to near dryness.
9. Add 2 ml of 16*M* HNO_3, and evaporate to near dryness.
10. Repeat step 9.
11. Add 2 ml of HNO_3, transfer each solution to a 10-ml volumetric flask with distilled water, and dilute to the mark with distilled water.
12. Allow the solutions to cool; dilute each to volume and shake.
13. Transfer 6 ml of each solution to a polyethylene sample cell and secure a sheet of Mylar over the open end with two O-rings.
14. Place each cell in the x-ray spectrograph in turn, and excite the solution using the molybdenum target x-ray tube.
15. Measure the intensities of the platinum $L\alpha_1$ and iridium $L\alpha_1$ x-ray lines.
16. Calculate the iridium-to-platinum intensity ratio for each solution using the equation

$$\text{intensity ratio, } R = \frac{\text{counts/s, Ir}}{\text{counts/s, Pt}} .$$

17. Calculate the slope, b, of the calibration curve for the known solutions using the equation

$$b = \frac{N\,\Sigma(\text{mg Ir} \times R) - (\Sigma\ \text{mg Ir})(\Sigma\ R)}{N\,\Sigma(\text{mg Ir})^2 - (\Sigma\ \text{mg Ir})^2} ,$$

where mg Ir is the weight, in milligrams, of iridium added to each known solution, R is the measured intensity ratio for each known solution, and N is the number of known solutions.

18. Calculate the intercept, a, of the calibration curve for the known solutions using the equation

$$a = \frac{\Sigma\ R - b\ (\Sigma\ \text{mg Ir})}{N} .$$

19. Determine the weight of iridium in each sample using the equation

$$\text{wt Ir, mg} = \frac{R - a}{b} ,$$

where R is the intensity ratio for the sample solution.

20. Determine the concentration of iridium in each sample using the equation

$$\text{Ir, \%} = \frac{\text{wt Ir, mg}}{\text{wt sample}} \times 100 .$$

VI. EXPERIMENTAL

Fusion. Various fluxes, including oxidizing alkaline fluxes, have been applied to the dissolution of platinum metals and alloys. Iridium metal is reported to be more readily attacked by NaOH than is rhodium.[3] As LiH is converted to LiOH and Li_2CO_3 when heated in air, an effective flux is formed from the sample matrix. This fac-

was used in developing a satisfactory fusion-dissolution method. A 500-mg sample of LiH or LiD containing up to 20 mg of iridium is fused at 873°K for 2 h in a nickel crucible. After cooling, the residue, which includes the iridium salts, dissolves readily in HCl. However, dissolution of the residue in HNO_3 produces an iridium oxide that cannot be dissolved completely.

Selection of Solvent and Internal Standard. After dissolution of the residue, HCl is evaporated by several fumings with HNO_3. Using HNO_3 rather than HCl as the solvent for x-ray spectrographic measurements results in a more reproducible matrix because the mass absorption coefficient of HNO_3 is similar to that of H_2O, and therefore acid concentration is not critical.

Platinum is added to serve as an internal standard. Use of this internal standard minimizes other matrix and instrumental fluctuation effects and allows more latitude in sample size.

VII. RELIABILITY

Precision. Homogeneous samples of LiH and LiD containing known amounts of iridium were not available. The precision of the method was calculated from data obtained by analyzing, according to the recommended procedure, samples of LiH to which were added known amounts of iridium as $IrCl_3$ in HCl solution. Relative standard deviations (Table I) ranged between 2.3 and 0.4% for determining 1.4 to 10 mg of iridium. The plot of Ir/Pt intensity ratio vs concentration was linear over the range of 1 to 20 mg of iridium.

Accuracy. In the absence of standard reference materials, the bias of the method could not be unquestionably determined. Using chemical reference materials similar to the samples to calibrate the method should effectively eliminate any bias.

Interferences. The most serious interference in x-ray fluorescence analysis generally is caused by line overlap.

TABLE I

PRECISION OF MEASURING IRIDIUM IN LiH
(500-mg Samples)

Ir Added (mg)	Standard Deviation (mg)	Relative Standard Deviation (%)
1.41	0.032	2.3
2.50	0.010	0.4
4.96	0.063	1.3
9.80	0.055	0.6

TABLE II

ELEMENTS THAT MAY INTERFERE WITH THE $L\alpha_1$ LINES FOR PLATINUM AND IRIDIUM

Element	Line	Relative Intensity (Ref. 4)	Angle, °2θ, LiF (Ref. 4)
Pt	$L\alpha_1$	100	38.05
Ir	$L\alpha_1$	100	39.22
Zn	$K\beta_1$	30	37.54
Hf	$L\beta_5$	30	37.60
W	$L\beta_4$	20	37.72
Ta	$L\beta_3$	30	37.87
Er	$L\gamma_3$	10	38.11
Tm	$L\gamma_1$	40	38.14
Bi	Ll	30	38.17
Er	$L\gamma_2$	10	38.29
Ho	$L\gamma_4$	10	38.35
Ta	$L\beta_1$	80	38.47
Hf	$L\beta_2$	60	38.47
Os	$L\eta$	10	38.50
Ga	$K\alpha$	150	38.86
Ta	$L\beta_4$	20	39.04
Pb	Ll	30	39.16
Hf	$L\beta_3$	30	39.25
Er	$L\gamma_1$	40	39.59
Lu	$L\beta_2$	60	39.77
Ho	$L\gamma_2$	10	39.80
Re	$L\eta$	10	39.89
Hf	$L\beta_1$	80	39.89
Dy	$L\gamma_4$	10	39.89

Elements that may interfere with the determination of iridium when platinum is used as an internal standard are summarized in Table II. Only those x-ray lines within two line half widths (0.70° 2θ) of the $L\alpha_1$ lines for platinum and iridium and having a relative intensity of 10 or greater were considered.

The elements yttrium, silver, europium, thulium, lutetium, and gold may be present in the samples, and small amounts of nickel also may be introduced during the fusion process. The only possible interference would be expected from thulium by overlap of the $L\gamma_1$ line with the platinum $L\alpha_1$ line and from lutetium by overlap of its $L\beta_2$ line with the $L\alpha_1$ line of iridium. Samples containing between 0 and 10 mg of iridium, 4 mg of platinum, and 0 to 10 mg of thulium or lutetium were prepared in triplicate, and the intensities of the iridium and platinum x rays were measured. Serious interference in determining iridium was not observed with 5 mg of thulium or lutetium.

In the presence of 10 mg of thulium, iridium recoveries were approximately 0.3 mg low, and in the presence of 10 mg of lutetium, iridium recoveries were approximately 0.2 mg high. Therefore, if samples weighing 500 mg contain greater than 1% thulium or lutetium, these elements should be added to standards to eliminate interferences.

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