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DETERMINATION OF URANIUM DIOXIDE IN STAINLESS STEELS BY THE X-RAY FLUORESCENCE METHOD

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ABSTRACT

This paper describes a rapid method for the determination of uranium dioxide in stainless steel by direct X-ray fluorescent analysis after chemical solution of the sample in perchloric acid. Strontium is used as an internal standard.

X-ray fluorescence methods of analysis have many advantages over the commonly used chemical methods such as the colorimetric, gravimetric and volumetric, because elements which ordinarily interfere need not be separated before analysis.

Statistically, eleven independent solutions were counted and nine sets of results were obtained on each one. Standard deviations are shown.

I. INTRODUCTION

In the fabrication of fuel elements for an experimental reactor, uranium dioxide and powdered stainless steel, Type 304, are mixed and then encased in stainless steel plates. The problem of determining the amount of UO_2 in the finished fuel elements was complicated by the amount of stainless steel present. Gravimetric and volumetric procedures involved long and tedious separations. Direct colorimetric procedures were unsuccessful because of the interference of iron[1] and nickel.[2]

X-ray fluorescence techniques were examined as a means of solving the problem. Direct radiation of the uranium in the steel-encased sample by X-rays was inapplicable as the stainless steel case prevented the penetration of the X-rays to the uranium layer. Thus, the sample would have to be altered in some manner and the simplest procedure was to prepare an aqueous solution of the sample.

Birks and Brooks[3] analyzed uranium in solution by X-ray fluorescence, but their technique required evaporation of aliquots of the solution and analysis of the dry residue. Pish and Huffman[4] determined uranium in aqueous and in organic solutions extracted from raw materials. Predominant amounts of iron, chromium and nickel were not present.

This paper describes a rapid method for the determination of uranium dioxide in stainless steel by chemical solution of the sample and by direct X-ray fluorescence analysis of the resulting perchloric acid solution, without further separations or processing.

II. APPARATUS AND REAGENTS

The apparatus used in this laboratory consists of a North American Phillips X-ray spectrograph Type No. 12049 and milliampere stabilizer Type No. 52204 with an FA60 tungsten target X-ray tube and a lithium fluoride analyzing crystal. The X-ray tube was operated at 50 kv and 30 ma. A scintillation counter was used to record the counts. The solution cell was previously described.[5]

It is important that the space between the scintillation counter and the collimator as well as the collimator itself be shielded with lead in order to prevent pick-up of scattered radiation by the counter. Figure 1 shows a diagram of this shielding.

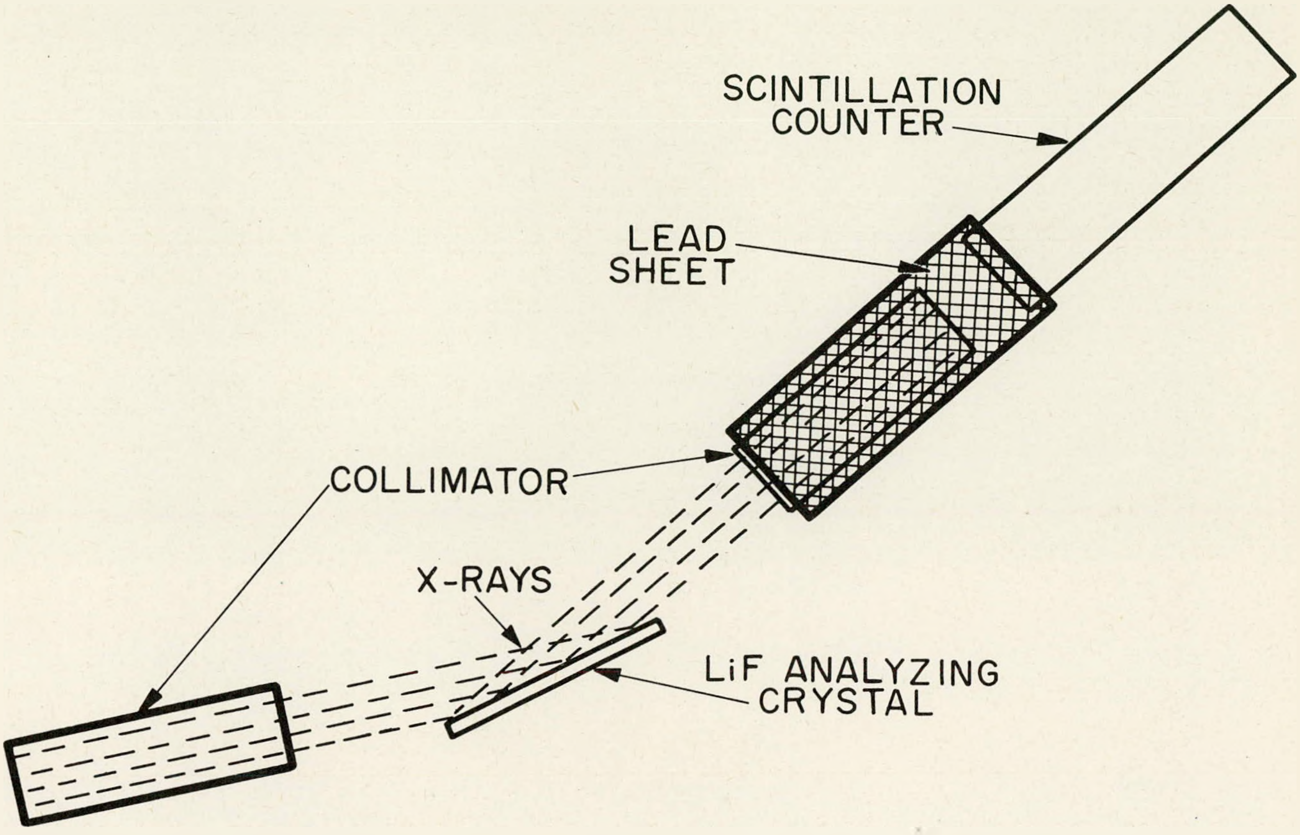

Fig. 1. Diagram of the Shielding of the System with Lead

Reagent grades of hydrochloric, hydrofluoric, nitric and perchloric acids were used to dissolve the samples. Chemically pure strontium nitrate was used to make the internal standard stock solution: 100 mg $Sr(NO_3)_2$ per ml of solution.

III. EXPERIMENTAL PROCEDURE

A. STANDARD WORKING CURVE

Perchloric acid solutions of synthetic mixtures of uranium dioxide and stainless steel were prepared. An internal standard of strontium nitrate was added to the solutions. The time required to record 204, 800 counts was measured for the K-alpha line of strontium and the L-alpha line of uranium. The ratio of counting time of strontium to counting time of uranium was calculated and plotted against the concentration (mg/ml) of uranium to form the working curve for uranium (Fig. 2).

B. SAMPLE PREPARATION

The sample of the uranium dioxide-stainless steel compact weighing about one gram was dissolved in 20 ml of a mixture of nitric and hydrochloric acids. Several drops of hydrofluoric acid and 15 ml of perchloric acid were added and the solution was evaporated until dense fumes of perchloric acid were given off. The solution was cooled and 2 ml of the standard strontium nitrate solution were added. The perchloric acid solution was transferred to a 100-ml volumetric flask and diluted to the mark with water. Approximately 10 ml of this solution was used to fill the solution cell. The time (40 to 60 seconds) to record 204, 800 counts was measured for the K-alpha line of strontium and the L-alpha line of uranium. The ratio of counting time of strontium to uranium was calculated and the mg/ml concentrations of uranium were obtained from the previously prepared working curve.

IV. RESULTS

Uranium dioxide can be dissolved in nitric acid but the presence of the stainless steel necessitated the use of aqua regia to put the samples in solution. The hydrofluoric acid was used to break up the insolubles and the perchloric acid was used to boil out the hydrochloric, hydrofluoric and nitric acids.

The use of the internal standard was required to approach the accuracy needed in the analysis. Without the use of the strontium as an internal standard,

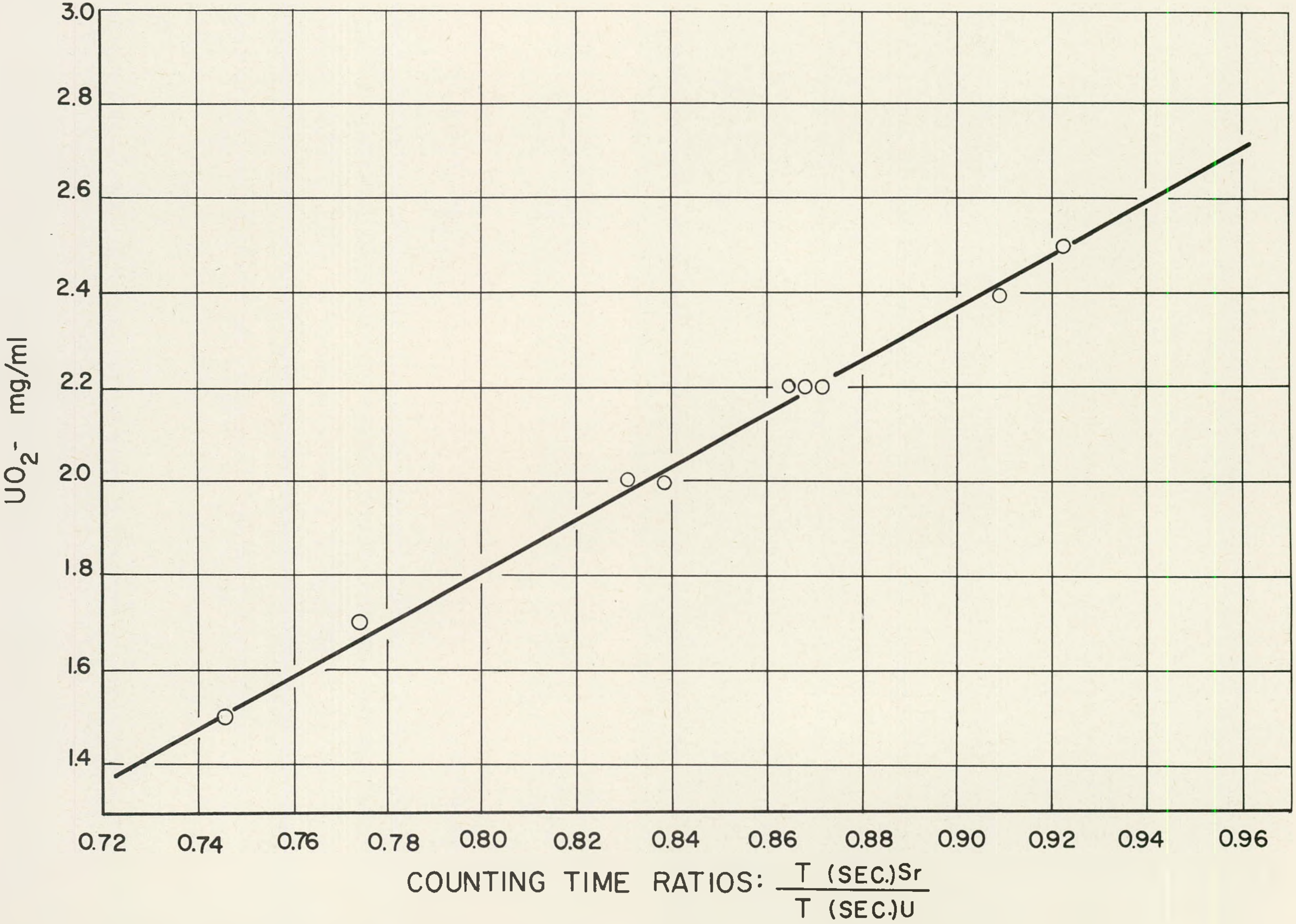

Fig. 2. Working Curve for Determination of Uranium by X-Ray Fluorescence Strontium as Internal Standard

the ratio of uranium to background would give results with an accuracy of about 5 per cent.[6] With the use of strontium, the reproducibility improved to approximately 2 per cent of the amount of uranium dioxide (15 ± 0.3) present. Any interelement effect is eliminated by adequate dilution of the sample.[6]

The lead shield as shown in Fig. 1 improved the ratio of uranium to background by a factor of 2.

The standard working curve of uranium dioxide (mg/ml) versus the counting time ratio of strontium to uranium is shown in Fig. 2. In Table I several wet chemical checks of the X-ray method are shown. The results of a series of measurements on several standard solutions are shown in Table II. In Table III are shown the counting statistics of a UO_2 - stainless steel standard solution

The correction of the uranium and of the strontium counting times for background counts did not improve the precision of the results. Doubling the concentration of the stainless steel in the solutions also had no effect on the intensity ratios of uranium to strontium.

The variation of intensity of the L-alpha line of uranium in the range 1.5 to 3.0 mg/ml was of such magnitude that a scintillation counter was required to obtain the required precision in these analyses.

TABLE I

COMPARISON OF X-RAY AND CHEMICAL METHODS FOR THE DETERMINATION OF URANIUM OXIDE IN STAINLESS STEEL

Sample No.	UO_2 Per Cent	
	X-Ray	Wet Chemical
1	17.6	17.3
2	15.8	15.9
3	15.4	15.5
4	16.2	16.3
5	16.5	16.2
6	15.2	15.2
7	15.0	15.1
8	15.8	16.0
9	16.0	15.8

TABLE II

ACCURACY OF RESULTS

Sample (%UO_2)	Number of Readings	Average I_U/I_{Sr}	Standard Deviation in Ratio	Standard Deviation (% UO_2)	UO_2 in Solution (mg/ml)
15.0	9	0.746	0.0074	0.42	1.5 ± 0.042
	9	0.746	0.0058	0.33	1.5 ± 0.033
17.0	9	0.774	0.0061	0.35	1.7 ± 0.035
20.0	9	0.832	0.0072	0.41	2.0 ± 0.041
	9	0.838	0.0055	0.31	2.0 ± 0.031
22.0	9	0.866	0.0066	0.37	2.2 ± 0.037
	9	0.868	0.0043	0.24	2.2 ± 0.024
	9	0.872	0.0042	0.24	2.2 ± 0.024
24.0	9	0.909	0.0092	0.52	2.4 ± 0.052
	9	0.909	0.0066	0.37	2.4 ± 0.037
25.0	9	0.922	0.0058	0.33	2.5 ± 0.033

TABLE III

COUNTING STATISTICS FOR A 17 PER CENT URANIUM OXIDE-STAINLESS STEEL SOLUTION

Average Ratio = 0.774

Standard Deviation = 0.0061

Standard Deviation expressed as % UO_2 = 0.34

Reading No.	Time to Record 204, 800 Counts (Seconds)		Ratio	Difference From Average Ratio	Difference (% UO_2)
	Sr	U			
1	30.7	39.7	0.773	0.001	0.06
2	31.0	40.0	0.775	0.001	0.06
3	30.7	40.0	0.768	0.006	0.34
4	31.4	40.3	0.779	0.005	0.29
5	31.6	40.4	0.782	0.008	0.46
6	31.6	41.0	0.771	0.003	0.17
7	31.6	41.4	0.763	0.011	0.63
8	32.0	41.0	0.780	0.006	0.34
9	32.0	41.2	0.777	0.003	0.17

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