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POLAROGRAPHIC ANALYSIS OF URANIUM

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## POLAROGRAPHIC ANALYSIS OF URANIUM

By G. H. Tishkoff

The polarograph has proved to be a practical and rapid method of analysis of  $U_4$  salts and  $UO_2$  for amount of  $U_6$  present as impurity.

### THEORY

The theory underlying the procedure depends upon the solubility of yl which is dissolved from the sample by boiling in 0.1N HCl. The boiled solution is cooled to room temperature, deoxygenated with pure nitrogen, and analyzed with the polarograph. The height of the first polarographic reduction wave thus obtained is a direct function of concentration of yl and in a given determination is compared to a "standard" yl wave. The first polarographic yl wave occurring at approximately  $-0.20$  volt (based on the saturated calomel electrode) in 0.1N HCl is used for analysis, because this wave has been shown to obey the Ilkovic equation for diffusion current. An excellent discussion of the theory underlying polarography and the Ilkovic equation is given by Müller.<sup>1</sup>

### APPARATUS

The polarograph used in this laboratory is the Sargent-Heyrovsky polarograph (Model XI). This model automatically records the current-voltage curves on photographic paper, whereby a permanent record may be obtained. By suitable adjustment of the galvanometer and camera, seven to nine polarograms (current-voltage curves) may be obtained on a single record.

The nitrogen is purified by washing with Fieser's solution.<sup>2</sup>

The dropping mercury cell consists of a round-bottom pyrex tube 2.8 cm in diameter and 8 cm in length. A saturated KCl calomel cell is connected to the dropping mercury cell by means of a saturated KCl agar bridge. The mercury capillary (supplied by Sargent Co.) is 10 cm in length.

The mercury (purified and redistilled in this laboratory) is maintained at a constant height with a leveling bulb. It is very important that the mercury height be maintained at a constant level during the analysis.

All rubber stoppers and connections are made sulfur-free by boiling with 20 per cent NaOH.

The apparatus is set up so that the nitrogen outlet from the dropping mercury tube is inserted into another cell in which a second sample is being prepared for analysis. This arrangement permits the preparation of the second sample while the first one is being analyzed with the polarograph.

<sup>1</sup>Müller, O. R., *The Polarographic Method of Analysis*, Jour. Chem. Edu., 1941.

<sup>2</sup>Fieser, *Experiments in Organic Chemistry*, p48, Heath and Company, New York, 1935.

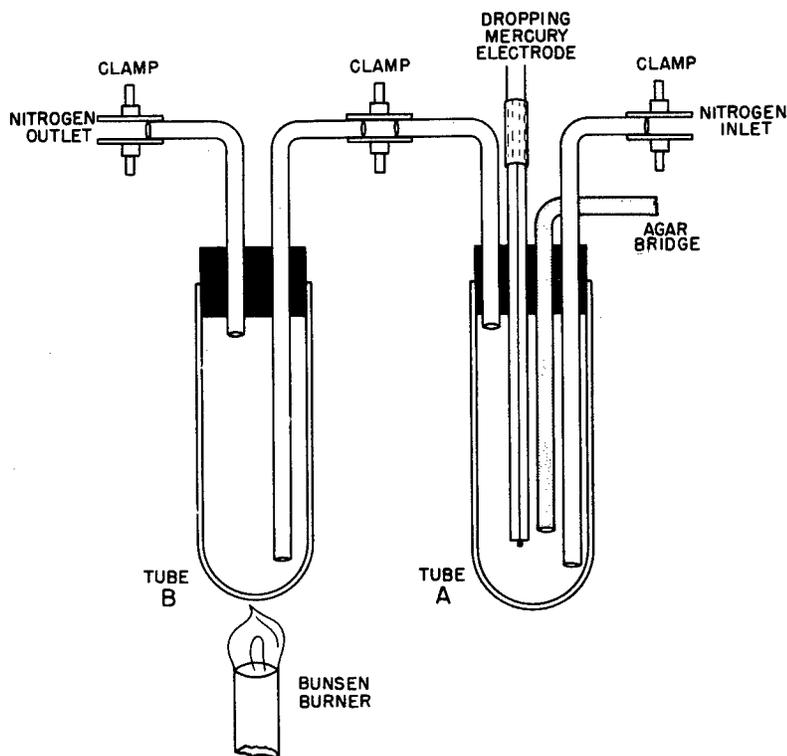


Figure 1.

#### PROCEDURE

Figure 1 shows a diagram of the setup employed. Ten ml of the standard solution (0.001M K in 0.1N HCl) is placed in the dropping mercury cell (A) and nitrogen passed through for 15 minutes. During this time 10 ml of 0.1N HCl is pipetted into sample tube (B) connected to the nitrogen outlet of (A), and the contents of this tube are heated to boiling. A constant flow of nitrogen is maintained through both tubes (A) and (B) until tube (B) has cooled to room temperature (approximately 15 minutes). Since no nitrogen can pass through the dropping mercury cell (A) when the polarogram is made, tube (B) is sealed from the atmosphere with a suitable clamp arrangement while the polarogram is being run.

After the polarogram is made, the standard solution is removed and the electrodes and agar bridge are washed down with distilled water. The tube containing the sample, which has now sufficiently cooled, is connected to the mercury electrode and the procedure is repeated with another sample. The total time during which nitrogen is passed through each individual solution is 30 minutes. Usually two runs are made on each sample or material to be analyzed, using a freshly weighed portion for the duplicate analysis. Figure 2 illustrates typical results.

## CALCULATION

A = height of standard wave

B = height of sample wave

$$(.001) \frac{B}{A} = C \text{ (conc of } U_6 \text{ in solution)}$$

$$\frac{C (270)}{100} = D \text{ (grams } UO_2^{++} \text{ in 10 ml)}$$

$$\frac{D \times 100}{\text{weight of sample}} = \text{per cent } UO_2^{++}$$

## RESULTS

The industrial samples of "green" salt submitted to us for analysis have been found by polarographic analysis to contain from 1 to 3 per cent  $UO_2^{++}$  by weight. The deviation for an averaged value of duplicate analyses of an individual sample is less than plus or minus 3 per cent, and deviations less than plus or minus 2 per cent can be obtained if larger samples are used.

## DISCUSSION

The polarographic method has numerous advantages over other methods for analysis of  $U_6$  in the

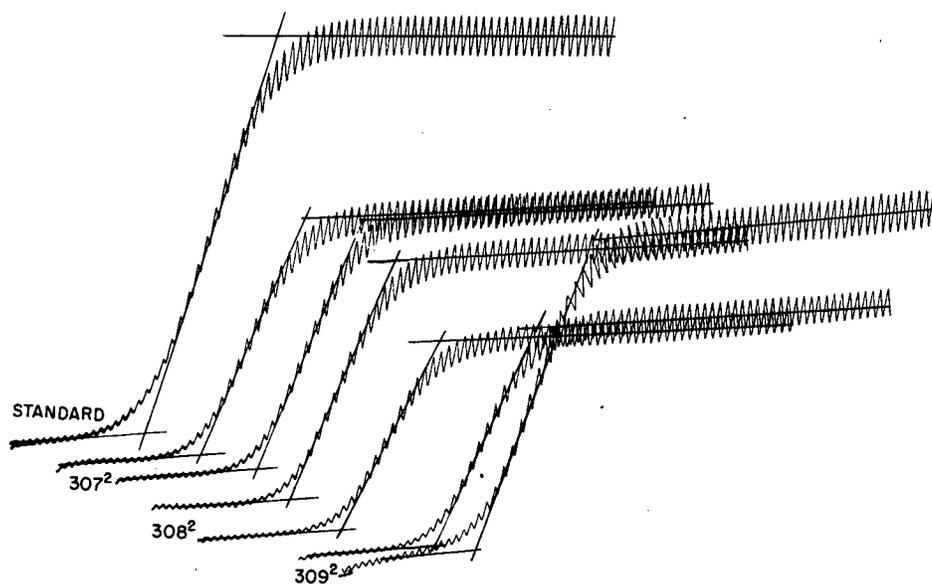


Figure 2.

green salt. No lengthy analytical methods are needed to separate the  $U_6$  from  $UF_4$  since the very small amount of precipitate present does not interfere with the dropping mercury electrode. Also, the method is a direct method. The usual chemical procedure is to extract  $U_6$  and analyze for  $U_4$  by volumetric methods. Then total U must be determined, and the  $U_6$  found by subtraction. Thus, relatively small percentage errors in the determination of  $U_4$  and total U can cause gross errors in the analysis of small amount of  $U_6$  which is determined by the difference between total U and  $U_4$ .

With the polarograph, a technician can easily analyze eight to ten samples a day if two runs are made on each sample. The method also provides a permanent record of the results.

#### SCOPE OF METHOD

This method of analysis has already been applied successfully to green salt and to  $UO_2$ . It can probably be applied to the analysis of any insoluble  $U_4$  salt for  $U_6$ . Moreover, soluble  $U_4$  salts can be analyzed for  $U_6$ , since the dissolved  $U_4$  does not interfere, and any soluble  $U_6$  salts may be analyzed readily for total U.