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# THE MEASUREMENT OF THE SURFACE AREA OF URANIUM DIOXIDE POWDER

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## The Measurement of the Surface Area of Uranium Dioxide Powder\*

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A comparative method has been developed for the determination of surface areas of  $\text{UO}_2$  powder. The method depends on the sorption of phosphate ions from a solution containing P-32 labeled  $\text{NaH}_2\text{PO}_4$  on the powder surface. By comparison with samples of known surface area, measurements have been obtained in the range 1.0-14 meter<sup>2</sup>/gm. The internal consistency of the method is better than  $\pm 2\%$  and agreement with measurements by the BET method averages around  $\pm 5\%$ . The method is simple and fairly rapid, and can be adapted to irradiated material.

### INTRODUCTION

The specific surface area of  $\text{UO}_2$  powder is one of the factors which control the sintering properties of the powder in the fabrication of reactor fuel rods. In general, a high sinter density can be achieved from powders having a large specific surface area (1). A minimum of about 3-4 meters/gm is required to approach the theoretical  $\text{UO}_2$  density of 10.97 gm/cc (2, 3) in any technologically acceptable sintering cycle.

A number of methods can be used to measure the specific surface area of powders (4). Among the most common methods in routine analyses are those depending on sorption onto the surface of the powder, or on air permeability through the powder. The sorption can be either from a gas or from a liquid. The gas methods are based on sorption of a gas, e. g., nitrogen, the inert gases, or hydrocarbons, at low temperatures. The basic principle of all the gas adsorption methods is that proposed by Brunauer *et al.* in 1938 (5). Although very reliable (6), and applicable to many types of powder (in a range from 50 cm<sup>2</sup>/gm (7) up to a few thousands of square meters per gram), the method is still relatively complex in spite of many recent improvements in technique.<sup>1</sup> For this reason it was felt

worthwhile to explore the possible use of liquid sorption methods for rapid relative determinations of surface areas.

Surface area determinations depending on sorption from a liquid are generally based on sorption of fatty acids from organic solutions. Although as accurate as the gas sorption methods (9), they do not have the same range of applicability. Moreover, they require fatty acids and solvents of the highest purity and, in certain cases, vacuum apparatus to desorb any gas from both the solution and the powder (4). Both types of sorption methods give an absolute value of the surface area, but depend on an accurate knowledge of the space occupied by a single molecule of the adsorbed species.

The gas permeability method, measuring the dynamics of a gas flow through a packed bed, gives only the surface area of the open pores. This means that for porous material having a large fraction of open, re-entrant pores the values of the specific surface area measured with the gas permeability method are generally lower than the values obtained with the sorption method (7). The present research resulted from an attempt to obtain a quick, simple method for measuring the specific surface area of  $\text{UO}_2$  powder in the range used for fuel-rod fabrication. However, it may also be used to measure a wider range of areas. It does not require any pre-treatment of the sample. The method is not absolute and is based on a comparison between the sorption of an active molecule—radioactive sodium dihydrogen

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<sup>1</sup> A gas sorption method has been used recently to determine the specific surface area of irradiated  $\text{UO}_2$  powder (8).



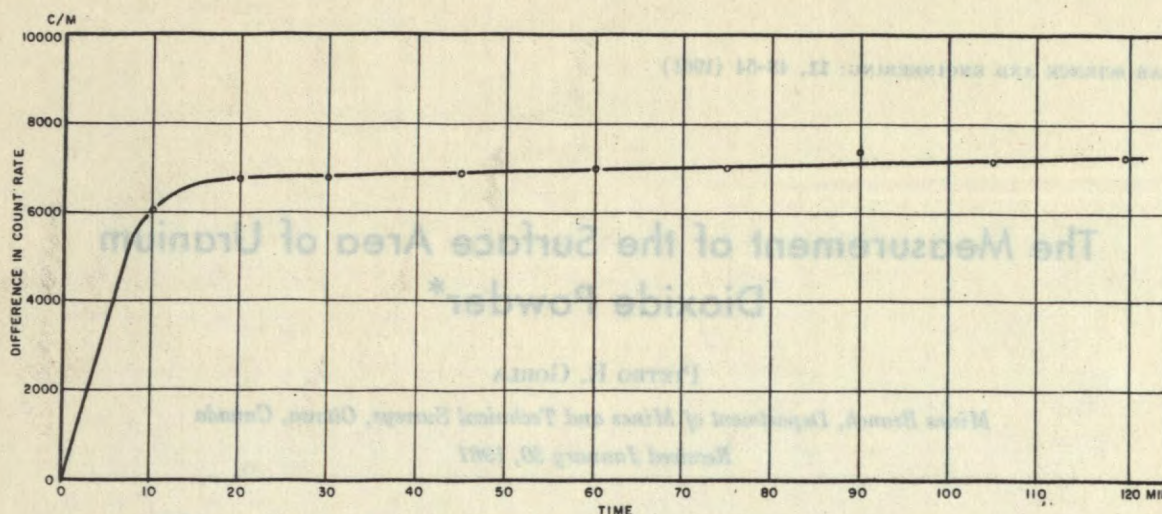


Fig. 1. Typical adsorption curve

orthophosphate—from an aqueous solution at room temperature on a reference sample and on the powder under examination.

#### THEORY AND PROCEDURE

Uranium dioxide has refractory properties and is attacked readily only by oxidizing agents. This implies that a medium-strength, nonoxidizing, nonreducing acid should adhere to the surface of  $\text{UO}_2$  without oxidizing or corroding it. A solution of sodium dihydrogen orthophosphate was found suitable for this purpose. A radioisotope of phosphorus, P-32, is readily available in high specific activity, carrier-free solutions as  $\text{H}_3\text{P}^{32}\text{O}_4$ . P-32 is a pure beta emitter ( $E_{\text{max}} = 1.71 \text{ Mev}$ ,  $T_{1/2} = 14.3 \text{ days}$ ), easily measured by a standard Geiger counter. These properties make the use of P-32 labeling very convenient as a means of measuring the phosphate concentration in a solution—one simply adds a known amount of the carrier-free  $\text{H}_3\text{P}^{32}\text{O}_4$  to the phosphate solution and then counts for a known period of time with a Geiger counter. Any decrease in the phosphate concentration can be followed by a proportional decrease in the counting rate. It has been observed that the reaction of phosphate ions, at room temperature, on  $\text{UO}_2$  powder is an irreversible reaction which, after an initial period of time, shows a very slight linear increase with time (Fig. 1). This increase is probably due to the building up of one or more layers of phosphate ions on the surface of the uranium oxide. It is evident that there is a threshold in the concentration of the solution, below which it would be impossible to cover the whole surface of a given amount of  $\text{UO}_2$ . A phosphate solution having a concentration somewhat above the threshold will show

a large change in the concentration following the sorption on  $\text{UO}_2$  powder. After a period of shaking sufficient for the reaction to reach the linear section of the curve (Fig. 1), the ratio of the change in P-32 concentration, due to a sample of unknown surface area, to the change in P-32 concentration with another sample of known surface area, is, within the accuracy of this method, equal to the ratio of the surface areas of the two powders.

#### EXPERIMENTAL PROCEDURE

One gram of  $\text{UO}_2$  powder, without any pre-treatment, was accurately weighed into each of four Lucite<sup>2</sup> test tubes. Two of the samples were the unknown powder, and two were reference powder samples of known (BET) surface area. The phosphate solution was a  $\text{NaH}_2\text{PO}_4$  solution with an activity of about  $2 \mu\text{C/ml}$  (for  $\text{H}_3\text{P}^{32}\text{O}_4$ ). Fifteen milliliters of this solution were poured very carefully into each test tube. Each test tube was then reproducibly positioned in a paraffin block at a fixed distance beneath an end-window Geiger counter (Fig. 2) and counted for 2 min. Due to the careful addition of the liquid over the powder in the test tube the  $\text{UO}_2$  remained at the bottom and did not affect the counting rate.<sup>3</sup> The first count was thus proportional to the

<sup>2</sup> In some preliminary experimental work, using glass test tubes, it was found that counting errors were introduced due to variations in the internal diameter of different test tubes. They were therefore replaced by Lucite test tubes which possessed a much more uniform cross section.

<sup>3</sup> Two centimeters of water are more than enough to stop all the beta and alpha particles from natural uranium. The Geiger counter, on the other hand, is relatively inefficient for detecting gamma radiations, which are usually low in intensity in purified  $\text{UO}_2$ .



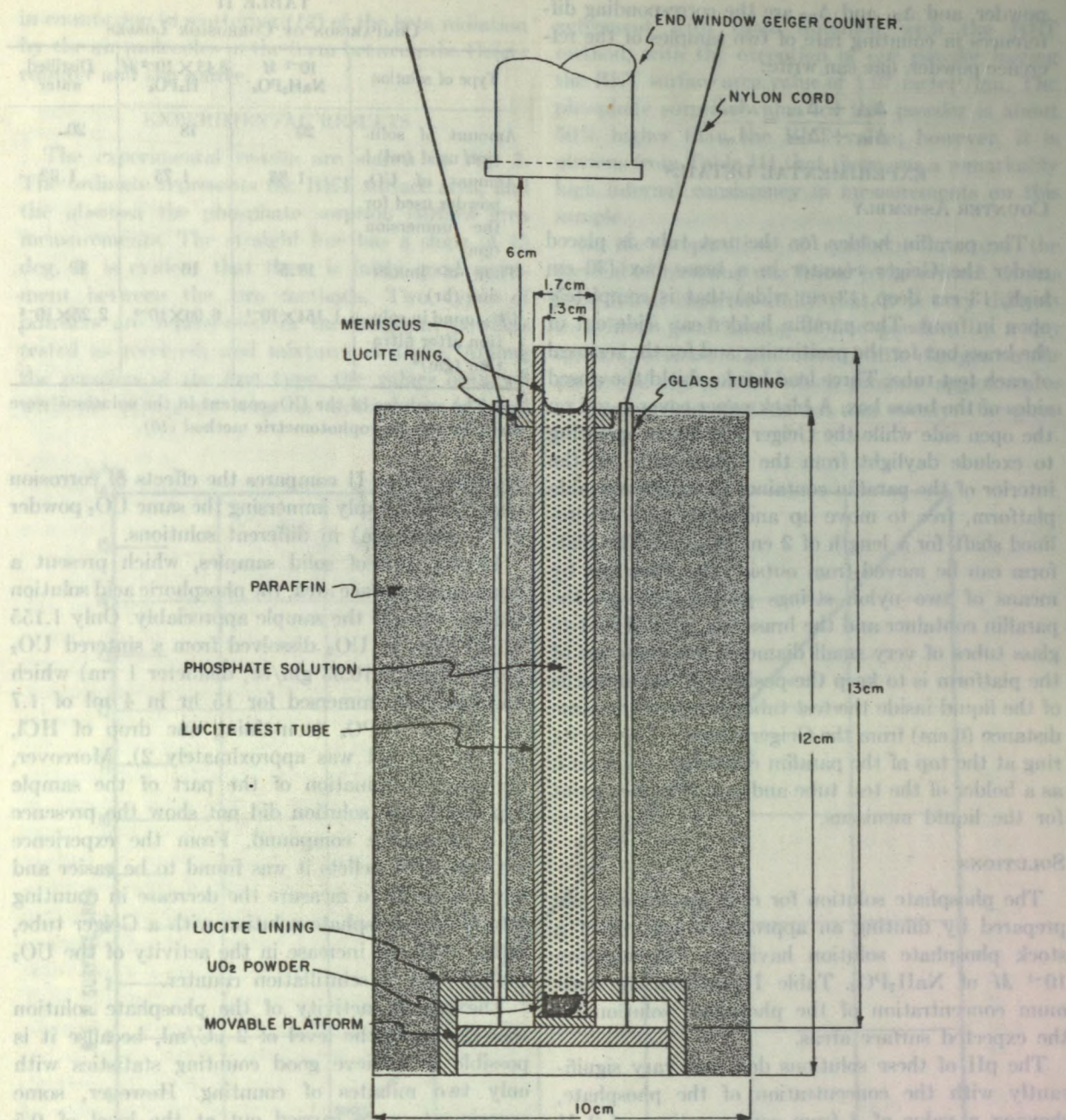


FIG. 2. Counter assembly

concentration of the solution before sorption. (This procedure was found more convenient in practice than the reverse one of adding known amounts of powder to the liquid and it was verified experimentally that no appreciable error was introduced from instantaneous sorption effects.)

After counting, the test tubes were closed with a polyethylene-covered rubber stopper and agitated for half an hour. This time was more than enough to reach saturation adsorption of phosphate on the

uranium dioxide powder. Following shaking, the test tubes were centrifuged for 10 min to remove the  $\text{UO}_2$  powder from suspension. The liquid phase in the tubes was then counted again for 2 min. The second count was proportional to the phosphate concentration after sorption. The difference between the two count rates was then proportional to the amount of phosphate adhering to the surface of the powder. If  $\Delta_{A1}$  and  $\Delta_{A2}$  are the differences in count rate before and after shaking for two samples of the unknown



powder, and  $\Delta_{B1}$  and  $\Delta_{B2}$  are the corresponding differences in counting rate of two samples of the reference powder, one can write:

$$\frac{\Delta_{A1} + \Delta_{A2}}{\Delta_{B1} + \Delta_{B2}} = \frac{A_{\text{test}}}{A_{\text{ref}}}$$

#### EXPERIMENTAL DETAILS

##### COUNTER ASSEMBLY

The paraffin holder for the test tube is placed under the Geiger counter in a brass box (30 cm high, 13 cm deep, 13 cm wide) that is completely open in front. The paraffin holder can slide out of the brass box for the positioning and for the removal of each test tube. Three lead bricks shield the closed sides of the brass box. A black paper cover is put on the open side while the Geiger counter is operating to exclude daylight from the Geiger tube. In the interior of the paraffin container there is a movable platform, free to move up and down in a Lucite-lined shaft for a length of 2 cm (Fig. 2). The platform can be moved from outside the brass box by means of two nylon strings passing through the paraffin container and the brass box, guided by two glass tubes of very small diameter. The function of the platform is to keep the position of the meniscus of the liquid inside the test tube always at the same distance (6 cm) from the Geiger counter. The Lucite ring at the top of the paraffin container serves both as a holder of the test tube and as a reference point for the liquid meniscus.

##### SOLUTIONS

The phosphate solution for each experiment was prepared by diluting an appropriate amount of a stock phosphate solution having a concentration  $10^{-1} M$  of  $\text{NaH}_2\text{PO}_4$ . Table I indicates the optimum concentration of the phosphate solution for the expected surface areas.

The pH of these solutions does not vary significantly with the concentration of the phosphate, showing a value of 4 from concentrations of 2  $M$  down to 0.03  $M$  of  $\text{NaH}_2\text{PO}_4$ . Corrosion of  $\text{UO}_2$  is not an important problem with this phosphate

TABLE II  
COMPARISON OF CORROSION LOSSES

Type of solution	$10^{-1} M$ $\text{NaH}_2\text{PO}_4$	$8.43 \times 10^{-2} M$ $\text{H}_3\text{PO}_4$	Distilled water
Amount of solution used (ml)	20	18	20
Amount of $\text{UO}_2$ powder used for the immersion (gm)	1.85	1.75	1.92
Time of immersion (hr)	18.5	10	10
$\text{UO}_2$ found in solution after filtration (gm) <sup>a</sup>	$1.154 \times 10^{-1}$	$6.06 \times 10^{-2}$	$2.25 \times 10^{-3}$

<sup>a</sup> The analyses of the  $\text{UO}_2$  content in the solutions were made by the fluorophotometric method (10).

solution. Table II compares the effects of corrosion observed by simply immersing the same  $\text{UO}_2$  powder (7.71 meter<sup>2</sup>/gm) in different solutions.

In the case of solid samples, which present a much lower surface area, the phosphoric acid solution did not corrode the sample appreciably. Only  $1.155 \times 10^{-6}$  gm of  $\text{UO}_2$  dissolved from a sintered  $\text{UO}_2$  pellet (density 10.53 gm/cc; diameter 1 cm) which had one side immersed for 15 hr in 4 ml of  $1.7 \times 10^{-2} M$   $\text{H}_3\text{PO}_4$  (containing one drop of  $\text{HCl}$ , so that the pH was approximately 2). Moreover, an x-ray examination of the part of the sample exposed to the solution did not show the presence of a phosphate compound. From the experience with the  $\text{UO}_2$  pellets it was found to be easier and more accurate to measure the decrease in counting rate of the phosphate solution with a Geiger tube, rather than the increase in the activity of the  $\text{UO}_2$  sample with a scintillation counter.

The specific activity of the phosphate solution was chosen at the level of 2  $\mu\text{C}/\text{ml}$ , because it is possible to achieve good counting statistics with only two minutes of counting. However, some experiments were carried out at the level of 0.5  $\mu\text{C}/\text{ml}$ , and at counting times of 10 min.

##### DETECTOR CHARACTERISTICS

The Geiger counter used in this work was a self-quenching end-window counter of type TGC-2. Its dead time was determined by the method of two sources (11). The two sources were  $\text{UO}_2$  sintered pellets of about 10 gm each, with an activity of about  $10^2$  counts/min each. The dead time was found to be 150  $\mu\text{sec}$ . No electronic quenching circuit was used with the Geiger counter. No corrections were applied to the counting results for the increase

TABLE I  
SUITABLE PHOSPHATE CONCENTRATIONS

Surface area (meter <sup>2</sup> /gm)	Concentration ( $10^{-2} M$ )
20	5
15	5-2.5
10	2.5
5	2.5-0.62
0.5	0.62-0.31

in counts due to scattering (12) of the beta radiation by the air molecules in the 6 cm between the Geiger counter and the source.

#### EXPERIMENTAL RESULTS

The experimental results are shown in Fig. 3. The ordinate represents the BET surface area, and the abscissa the phosphate sorption surface area measurements. The straight line has a slope of 45 deg. It is evident that there is fairly good agreement between the two methods. Two types of powders are represented in the diagram: powders tested as received, and mixtures of them. Among the powders of the first type, the values obtained with the phosphate sorption method are in good

agreement with those obtained with the BET method, with the exception of one powder having the BET surface area value of 1.97 meter<sup>2</sup>/gm. The phosphate sorption value for this powder is about 50% higher than the BET value; however, it is obvious from Table III that there was a remarkably high internal consistency in measurements on this sample.

In the preparation of synthetic mixtures the method of blending was found to be critical. It has been found experimentally that it is very difficult to achieve good mixing of fine powders by a dry method, because of the electrostatic charges on the surface of the powder which produce agglomerates of fine particles that do not mix evenly. One-gram

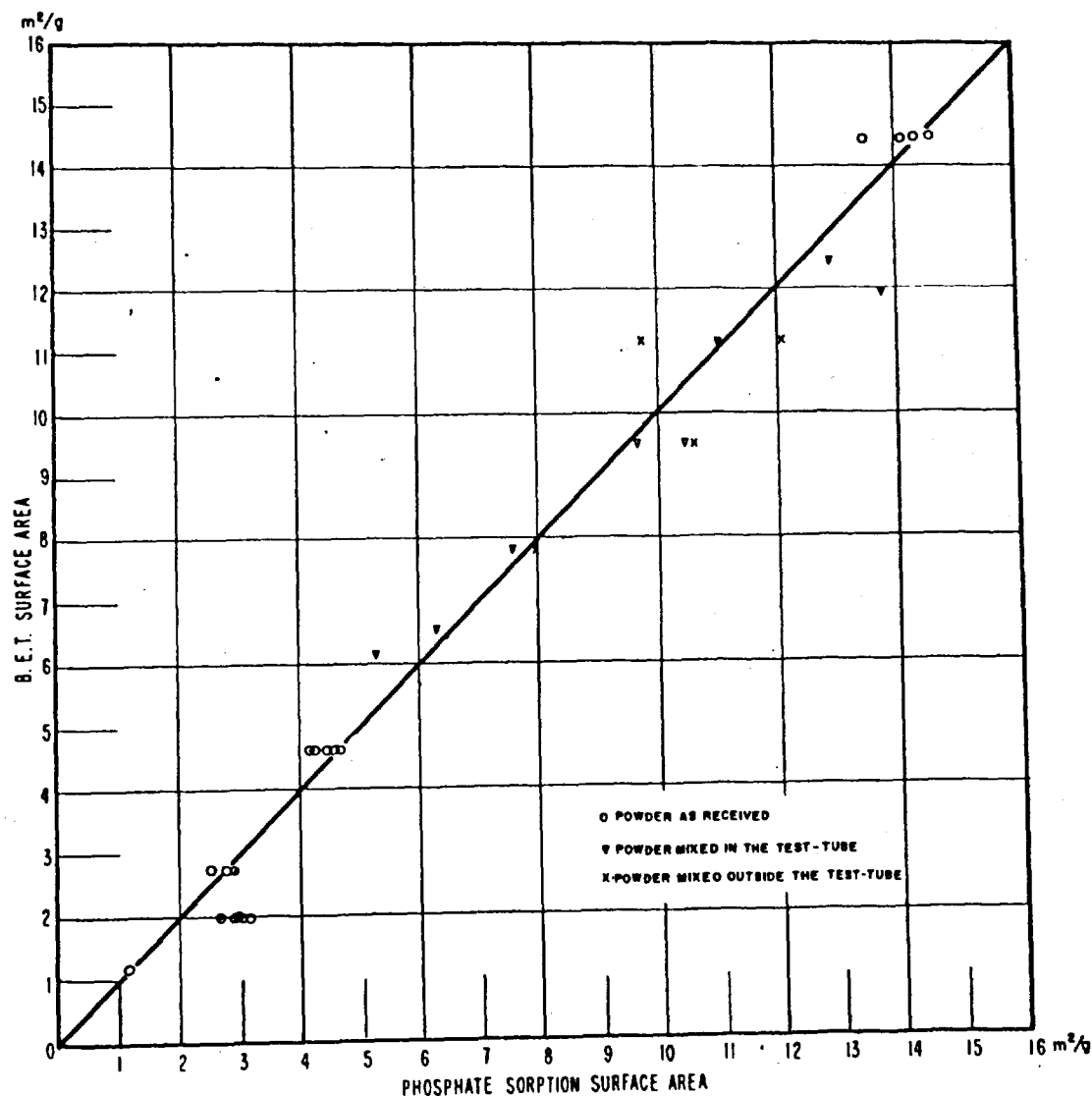


Fig. 3. Experimental results

samples taken from larger mixtures obtained by previous mixing of appropriate amounts of two powders showed bigger discrepancies from the BET surface area values than did those samples in which the two powders were merely combined in the same ratios up to 1 gm inside the test tube. This effect was clearly due to difficulties in obtaining truly representative samples for the former mixtures.

The internal consistency of the method is shown in Table III. It is seen to be better than  $\pm 2\%$  on the average. Table IV shows a comparison with the BET values of the results obtained with the phosphate sorption method for various powders, both those tested as received, as well as for synthetic mixtures mixed inside the test tubes.

TABLE III  
INTERNAL CONSISTENCY OF RESULTS

Experimental results (meter <sup>2</sup> /gm)	Average value	Percent error	Method of preparation <sup>a</sup>
1.06	1.04	1.28	A
1.02			A
3.13	2.94	2.2	A
2.82			A
2.63			A
2.97			A
3.15			A
2.75	2.69	1.98	A
2.54			A
2.80			A
4.50	4.40	1.26	A
4.15			A
4.23			A
4.18			A
4.45			A
4.68			A
4.64			A
10.43	10.03	2.5	B
9.64			B
14.35	14.13	1.05	A
14.12			A
13.50			A
14.54			A
Mean per cent error $\pm 1.7$			

<sup>a</sup> A = powders tested as received; B = powders mixed inside the test tube.

$$\text{Percent error} = \frac{\sqrt{\sum_i (\bar{x} - x_i)^2 / n(n-1)}}{\bar{x}} \times 100$$

where  $\bar{x}$  = average value, and  $n$  = number of runs per powder sample.

TABLE IV  
COMPARISON OF THE TWO METHODS

Number of the sample	Phosphate sorption surface area (average) (meter <sup>2</sup> /gm)	Number of runs	Method of preparation <sup>a</sup>	BET surface area (meter <sup>2</sup> /gm)	Percent deviation
1	1.04	2	A	1.06	-1.88
2	2.94	5	A	1.97	+49.3
3	2.69	3	A	2.75	-2.18
4	4.40	7	A	4.60	-4.35
5	5.26	1	B	6.15	-14.5
6	6.28	1	B	6.56	-4.27
7	7.52	1	B	7.86	-4.33
8	10.03	2	B	9.50	+5.58
9	11.04	1	B	11.13	-0.81
10	13.78	1	B	11.95	+15.3
11	12.90	1	B	12.44	+4.50
12	14.13	4	A	14.40	-1.87

<sup>a</sup> A = powders tested as received; B = powders mixed inside the test tube.

## DISCUSSION

The phosphate sorption method, based on the comparison between the sorption of an active phosphate ion on a reference sample of known surface area and on the powder under examination, does not require any pre-treatment of the powder itself. The internal consistency is fairly high, of the order of  $\pm 2\%$  as seen from Table III. The sampling is a crucial point. Due to the small amount of powder (1 gm) used, it must be free of large lumps which would introduce major errors in surface determinations. From this point of view, representative sampling is of major importance and sampling errors form the biggest factor in the discrepancy between the two methods, which has a mean value of  $\pm 5-6\%$ . It should be pointed out that the BET values were always taken as reference standards, which means that the accuracy given above is not absolute, but relative to that of the BET method, which itself is subject to errors of the order of  $\pm 3-5\%$ .

Experiments were performed to see if it was possible to measure the surface area of sintered  $\text{UO}_2$  pellets. The diffusion of the phosphate solution through the capillaries of the solid samples proved to be a very slow process compared with that of a gas, so that the surface area obtained was the geometrical area only. For that reason the phosphate sorption method appears to be less useful when dealing with sintered  $\text{UO}_2$  samples.

For routine work the system could be calibrated with known samples and the use of reference samples

could be restricted to periodic checks to allow for the decay of the P-32 activity in the stock solution.

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