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SURFACE AREA DETERMINATION OF MAGNESIUM POWDERS BY SORPTION OF C-14-LABELED OLEIC ACID

by

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MINERAL SCIENCES DIVISION

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SURFACE AREA DETERMINATION OF MAGNESIUM POWDERS BY SORPTION OF C-14-LABELED OLEIC ACID

by

C.M. Lapointe[*]

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SYNOPSIS

The chemisorption of C-14-labeled oleic acid on magnesium particles has been used to determine the surface area of the grains when this area is only a few hundred square centimetres per gram. A simplified technique is suggested for routine measurement of several samples a day.

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DÉTERMINATION DES SURFACES DE POUDRE DE MAGNESIUM PAR L'ADSORPTION D'ACIDE OLÉIQUE MARQUÉ AU C-14

par

C.M. Lapointe[A]

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RÉSUMÉ

On a utilisé la chémisorption d'acide oléique marqué au carbone-14 sur des particules de magnésium pour déterminer l'aire de leur surface, dans le cas où cette aire n'est que de quelques centaines de centimetres carrés par gramme. On suggère une simplification de la technique pour les mesures de routine.

[A] Chargé de recherches principal, Section de la physique et des indicateurs radioactifs, Division des sciences minérales, Direction des Mines, Ministère des Mines et des Relevés techniques, Ottawa, Canada.

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INTRODUCTION

In reactions between solids, or between solids and liquids, the initial rate of reaction is a function of the surface area of the solids. When the reaction is exothermic, as is the case in the reduction of certain oxides with powdered metal, a knowledge of the true areas in contact becomes necessary to prevent the reaction from getting out of control and turning into an explosion.

For surface areas of the order of square metres per gram, the B.E.T. gas adsorption technique (1) is well suited and gives reproducible results. However, when the areas to be measured are only a few hundred square centimetres per gram, a radiometric method seems indicated, because of its almost unlimited sensitivity. A technique using potassium dichromate labeled with chromium-51 has been described elsewhere (2). This paper deals with the monolayer adsorption of C-14-labeled oleic acid on magnesium particles, following the method proposed by Harkins and Gans (3), but substituting radiometric determinations for the less sensitive titrimetric measurements used by those authors.

It has been known for almost a century (4) that certain fatty acids tend to form a single layer of molecules on a water surface, and that the area at the interface covered by one molecule is independent of the number of carbon atoms in the molecule. This indicates that these molecules are quite straight and elongated, and that each is orientated vertically on a water surface. Adam's determinations (5) showed that each molecule occupies an area of 20.5 A^2. This property suggested to Harkins and Gans (3) that these molecules might also form a monolayer at the interface between a solid and a liquid, thus affording a technique for the measurement of the surface area of the solid.

EXPERIMENTAL DETAILS

The sorption method of surface area measurement is quite simple. A weighed amount of the magnesium powder is exposed to an oleic acid solution of known concentration, and a determination of the concentration of the acid in an aliquot after sorption gives the amount of acid adsorbed on the sample.

The Liquid Scintillation Apparatus

Since the C-14-labeled oleic acid used as the tracer cannot be conveniently measured with a flow-counter, the more efficient internal counting method in a liquid scintillator was adopted.

The measurements were performed in an apparatus similar to the one described in a previous report (7). The scintillator consisted of a solution in toluene of 3 grams per litre of PPO (2,5 diphenyl-oxazole), to which a small amount of

POPOP[A] had been added. In order to decrease the background and keep the sample close to the photomultiplier, a minimum amount of liquid, 10 ml, was used. A significant reduction in the thermal noise of the photomultiplier was obtained by placing the lead castle and the detector in a deep-freeze unit, where the temperature was maintained at -35°C. The pulses from the photomultiplier were fed through a pre-amplifier to a type 1820 Nuclear-Chicago spectrometer, and then to a scaler.

Preparation of the Oleic Acid Solution

When a radioactive substance is to be introduced into a liquid scintillator, the choice of the solvent is of primary importance because of the possible quenching effect on the scintillator's efficiency. Thus, while carbon tetrachloride, methanol, and ethanol have been employed as solvents for oleic acid in sorption measurements, toluene was chosen here because the scintillator used had a toluene base.

Some long-chain hydrocarbons have also been used as solvents in certain cases, but it has been shown (6) that at low oleic acid concentration such solvent molecules may become attached to the surface of the solid and thus indicate too low a value for the surface area, as measured by the amount of oleic acid adsorbed.

[A] 1,4-bis-[2-(5-phenyloxazolyl)]-benzene.

The radioactive tracer, as supplied by Merck and Co. Limited, Montreal, consisted of 70.6 mg oleic acid-1-C-14 with an activity of 0.5 mc. This corresponds to 1.85×10^7 disintegrations per second (dps). As an activity of about 100 dps was desirable in an aliquot of 100 μl of a solution containing about 25μg oleic acid per ml, the following dilution was carried out:

> The tracer was brought up to 5 ml with toluene, resulting in an activity of 3.7×10^3 dps per μl. 25μl of this tracer solution were added to 100 ml of a solution containing 2.5 mg of pure inactive oleic acid in toluene. This latter solution had been prepared by weighing out 250 mg of oleic acid and dissolving it in 100 ml of toluene, and then pipetting 1 ml of this dilution in 99 ml of toluene.

Thus, the solution to be used for adsorption measurements on magnesium contained 25 μg of oleic acid per millilitre and has an activity of 92.5 dps per 100 μl aliquot--a convenient activity for the apparatus used.

Although most of the tests were run with magnesium powder dried in a desiccator over Drierite, a few samples were also dried in a vacuum with application of gentle heat. The results showed no measurable difference attributable to the drying method.

Four millilitres of the stock solution were pipetted into a 10 ml glass vial fitted with an aluminum-lined plastic cap, and, after shaking for 2 hours in order to saturate the container walls, a 100 μl aliquot was pipetted out and measured in the liquid scintillator. Then a weighed amount of the magnesium powder was added to the vial and shaken for another 2 hours; another 100 μl aliquot was pipetted out, added to the liquid scintillator, and measured. The difference in net activity between the first and second readings gave the amount of oleic acid adsorbed.

The magnesium powder used was part of a sample that had been submitted by Mr. W.J. Craigen of Eldorado Mining and Refining Limited for surface area determination. It was fairly coarse, and the -28+35 mesh fraction was used throughout this work. A microscopic examination performed on it by Mr. S. Kaiman, mineralogist of the Extraction Metallurgy Division of the Mines Branch, supplied the following information:[A]

> "The magnesium consists of silvery metallic grains, which have a tendency to be flaky. When lying on a flat surface, the grains show smooth surfaces and edges, and the outlines are rounded and approach oval in shape. Rare grains are globular and almost hemispherical. The average radius is estimated to be approximately 2½ times the thickness."

Figure 1 shows a typical photomicrograph of the coarse powder.

[A] On December 4, 1959.

Figure 1. - Photomicrograph of a sample of the -28+35 mesh fraction of the magnesium powder. (X 10)

RESULTS

A series of four magnesium samples weighing respectively 0.25, 0.50, 0.75, and 1.00 gram gave the adsorptions indicated in Figure 2. The averaged value of four sets of these measurements corresponds to 80% adsorption per gram magnesium powder in 4 ml of the stock solution containing 25μg oleic acid per ml. It is to be noted that a one-gram sample of magnesium powder, shaken with only 2 ml of the stock solution, removed all of the oleic acid from the solution, thus indicating that the sorption is truly an irreversible, chemisorption phenomenon.

Taking 20.5 A^2 as the area covered by one molecule of oleic acid, the surface area in cm^2 per gram of magnesium powder is given by the formula:

$$\text{Surface area} = 20.5 \times 10^{-16} \frac{AN}{M}$$

where A = amount of oleic acid adsorbed per gram magnesium,

N = Avogadro's number, and

M = molecular weight of oleic acid.

So, for the -28+34 mesh fraction of powder under study, the surface area is found to be:

$$\text{S.A.} = \frac{20.5 \times 10^{-16} \times 80 \times 10^{-6} \times 6.023 \times 10^{23}}{282.46}$$

$$= 350 \text{ cm}^2/\text{g Mg.}$$

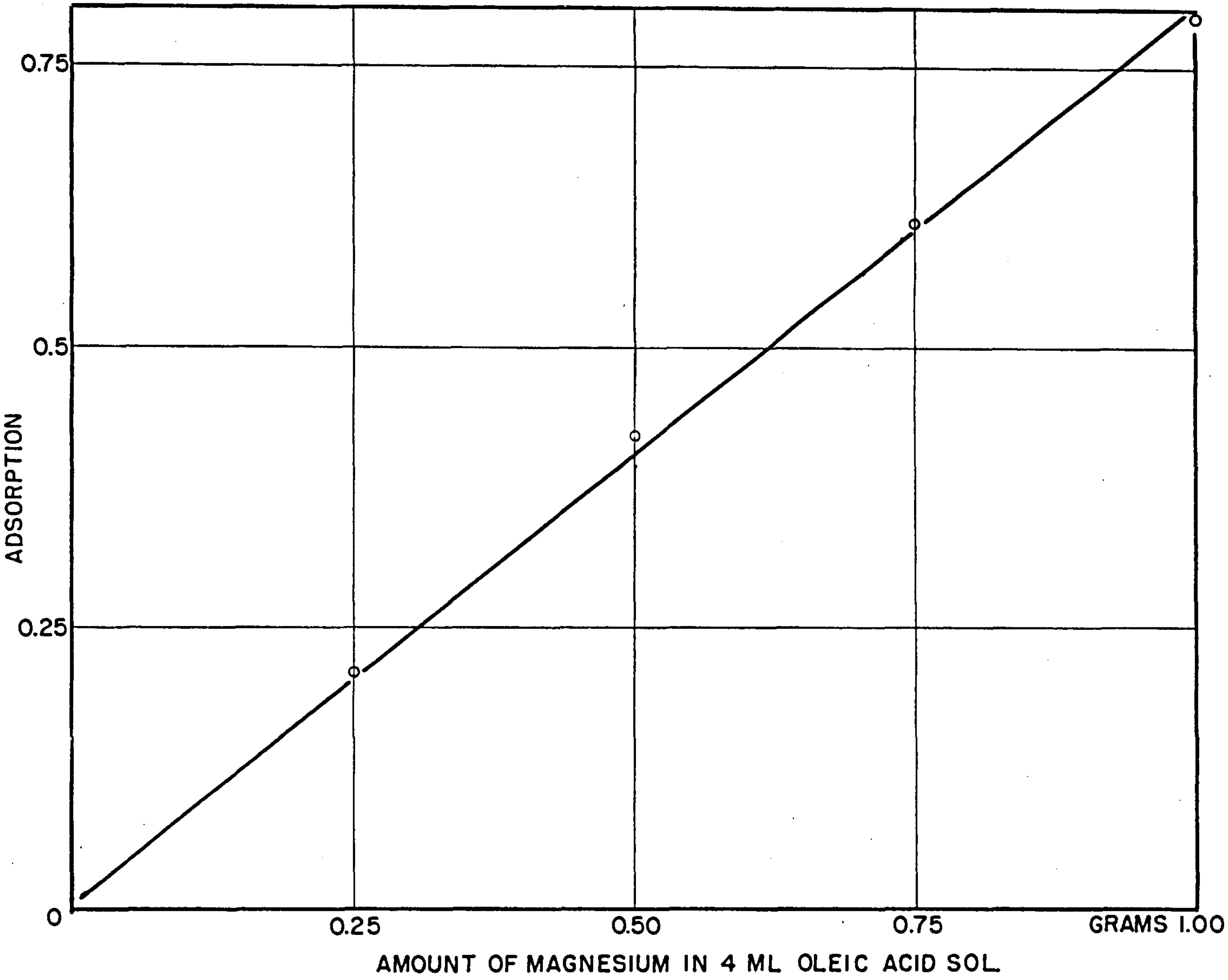

FIG. 2 - ADSORPTION CURVE FOR MAGNESIUM POWDER.

DISCUSSION OF THE RESULTS

The value obtained by this method, 350 cm^2/g, compares favourably with the one arrived at by the dichromate adsorption method (2), 280 cm^2/g. Indeed, because of some uncertainty in the determination of the surface area of the reference magnesium plates (2), the oleic acid value would be favoured, as being less dependent on a calibration by means of polished specimens.

However, the uncertainty in Adam's value for the specific area covered by fatty acids, the possibility of a small quenching effect in the scintillator due to the oleic acid, and the difficulties inherent to aliquoting very small amounts of liquid, may very well account for the difference in the results obtained with the two methods.

In the case where several samples have to be measured in one day, the method outlined here could be simplified by operating at room temperature. The amount of tracer used would have to be increased so as to compensate for a lower detector efficiency due to a higher discriminator setting. The contact period could be reduced from two hours to one, and the same scintillator could be used for up to ten samples without overloading the circuits.

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