U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 1, Project No. A-446-3
"An Investigation of the Use of Radioactive Isotopes for Determining the Surface Area of Powdered Materials by Sorption Methods"
Contract No. AT (38-1)-202
Task No. III, Contract Authorization No. IA-59-34
Covering the Period from April 1 to May 31, 1959

Gentlemen:

The objective of this research is the investigation of the use of radioactive tracer atoms in fatty acids or stearates in liquid solution as a means of accurate surface area measurements of low-surface materials.

The personnel involved in this research are Mrs. Margaret C. Kordecki, project director, and Miss Miriam Barnes, research assistant, who joined the project on April 22nd, after receiving her B. S. degree in chemistry.

During the months of April and May, work on this project has consisted of obtaining and purifying chemicals, obtaining new equipment and supplies necessary for the experimental work, and readying the equipment and supplies already available. One millicurie of stearic acid tagged with carbon-14 has been received. Appropriate end-window and gas-flow counters have been located for use in the new Radioisotopes and Bioengineering Building. Reagent grade benzene has been fractionally distilled and stored over sodium.

Several powders of known surface areas are available and will be used in this project. Utilizing these surface area values and the specific activity of the radioactive stearic acid, calculations have been made to determine the appropriate dilution of the carbon-14-tagged stearic acid with stearic acid that is not radioactive, in order to obtain sample counts within a desirable range.

Next month the experimental work will be initiated. The specific activity of solutions of stearic acid-1-C-14 in benzene will be determined by counting small aliquots from which the solvent has been evaporated. Several samples of one powder will then be stirred in stearic acid solutions of different concentrations and centrifuged to settle the powder. Small
aliquots of the supernatant liquor will be counted after evaporation of the solvent. From these counts, the specific activity and concentration of the stearic acid, and the size of the acid molecule, the surface area of the powder will be calculated.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division
During the month of June several experiments have been conducted to determine the best procedures for surface-area determinations by the use of stearic acid tagged with carbon-14. A sample of clay with a surface area of approximately $8 \text{ m}^2 / \text{gm}$ (determined previously by gas-adsorption methods) was used. Weighed samples of the oven-dried clay were placed in a gloved dry box, which is being used not only to keep moisture from the samples and reagents, but also to contain the radioactive material and avoid contamination of the laboratory. Inside the dry box the samples were stirred in benzene solutions of stearic acid, about 0.4 percent of which was stearic acid-C-14. They were then centrifuged in stoppered tubes, and samples of the supernatant liquor were transferred to small glass plates and allowed to dry. The plated samples were placed in aluminum planchets and counted with an end-window Geiger tube. Aliquots of the original stearic acid solution were also plated and counted, the difference between these and the sample counts being a measure of the stearic acid adsorbed.

Several different weights of clay which gave values from $2.7$ to $7.3 \text{ m}^2 / \text{gm}$ were used. The handling techniques must be improved so that duplication of results can be routinely obtained. The main source of error appears to be the method of plating samples for counting. Pipettes and hypodermic needles have been used, but handling these with rubber gloves is difficult. It is expected that the plating technique will be greatly improved by the use of automatic micropipettes which have been ordered. Other sources of error are related to the geometry of the counter. For example, each sample must cover exactly the same area on the glass plates with a uniform deposit. The tendency to form droplets which leave non-uniform deposits on the plates will probably be eliminated by determining the best reagents for cleaning the glass plates before placing the solution on them. Also, each sample must be placed in the same position with respect to the counter window. The present method of placing samples in the counter will be improved by making a holder to position the samples under the tube.
Work in the immediate future will consist of incorporating into the experimental procedure the improved methods of plating and counting described above. Only clay samples will be used until the technique for determining their surface areas has been perfected. Other powders will be used at a later date.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief, Chemical Sciences Division
During the month of August numerous aliquots of a benzene solution of carbon-14-tagged stearic acid have been plated and counted. Different methods of transferring measured aliquots and different types of plates have been tested to develop the best possible technique for plating samples. "Micropettes" -- automatic micropipettes calibrated to deliver exactly 0.1 ml -- were received and have been used to transfer aliquots to plates for counting. Results with these have been disappointing, however, as the delivered volume sometimes varies by as much as 5 per cent. A hypodermic syringe still seems to be the best instrument for measuring small volumes inside the gloved dry box.

Several 0.1-ml aliquots of the radioactive material were transferred to glass cells (3 mm high and 15 mm in diameter) mounted on microscope slides and dried at room temperature. When these were counted, wide deviations (as much as 50 per cent) were found. These deviations apparently were caused by some dissolving action of benzene on the cement used to attach the cells to the slides. Samples were also plated on rubber discs, which proved unsatisfactory because the amount of the solution absorbed by the rubber varied. Teflon discs with diameters of 20 mm (used earlier for 0.05-ml aliquots) were too small to accommodate 0.1 ml of the solution. Attempts to contain this volume of solution by spreading layers of Duco cement, Teflon paint, or other materials around the edge of the Teflon discs were unsuccessful because of the solubility of these materials in benzene. Larger discs of Teflon, 32 mm in diameter, were used successfully for plating 0.1-ml aliquots. Deposits on these plates were uniform in appearance, duplicate samples gave counts with 1.3 per cent average deviation, and the plates were reusable because of the ease of washing the radioactive material off Teflon.
Approximately 15 per cent of the total work has been accomplished. In the immediate future surface areas of several duplicate clay samples will be determined. Hypodermic syringes will be used to transfer 0.1-ml aliquots of the solutions to Teflon plates 32 mm in diameter.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division
U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 4, Project A-446-3
"An Investigation of the Use of Radioactive Isotopes for Determining the Surface Area of Powdered Materials by Sorption Methods"
Contract No. AT (38-1)-202
Task No. III, Contract Authorization No. 1A-59-34
Covering the Period from September 1 to September 30, 1959

Gentlemen:

As a result of experimental work and literature research during the month of September, it has been ascertained that the stearic acid solutions previously used in the surface area determinations were too dilute to give the true equilibrium value for adsorption of stearic acid by clay. A powder will reach its maximum adsorption of a fatty acid only after a certain value of $C/Co$, where $C$ is the concentration of the acid solution at equilibrium with a powder sample and $Co$ is the saturation concentration of the acid, has been attained. For ease of handling, plating, and counting samples, it is desirable to use as low concentrations of the fatty acid as possible without shifting the adsorption equilibrium below its maximum value. Therefore, for each different combination of powder, fatty acid and solvent used in these fatty-acid sorption determinations, an adsorption isotherm must be determined experimentally or obtained from the literature. For kaolin in benzene solutions of stearic acid, the value of $C/Co$ should be at least 0.3.

Use of the higher concentration of stearic acid brings new problems, since it requires incorporation of larger quantities of carbon-14-tagged acid in the test solutions. The result is that counts for 0.1-ml aliquots of both the original solution and the solution after exposure to a powder sample are very high, though the difference between the two is relatively small, especially in the case of powders with very low surface areas, e.g., $2m^2/gm$ or smaller.

Some of the discrepancy, occasionally as high as 10 percent, in counts from duplicate plates has been traced to irregularities on the bottom of the Teflon plates. These irregularities prevented the plates from lying perfectly flat in the counter. Also, the opening in the plate holder used in the counter was found to be slightly off center in relation to the Geiger tube.
During October, surface area determinations will be made on several different types of powdered materials at the stearic acid concentrations indicated by their respective adsorption isotherms (plots of surface area versus $C/C_0$).

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division
During the month of November a very satisfactory method of plating benzene solutions of stearic acid for radioactive assay was found and adopted for routine procedure. In this plating technique either small watch glasses or Teflon discs are chilled thoroughly in a refrigerator. Upon removal from the refrigerator they are placed on a bed of cracked ice to keep them cold while the solution is pipetted onto them. They are then returned to the refrigerator, where the lowered solubility of the solute and the slower evaporation of the solvent combine to produce stearic acid deposits of very uniform appearance. Average deviations of less than 2 per cent have usually been obtained by use of this plating technique.

Also during this period the magnetic stirrer was found unsatisfactory for stirring powder samples in stearic acid solution, since the considerable heat generated by this stirrer reduces adsorption of the fatty acid. It was replaced with a mechanical stirrer, with a rubber sleeve, inserted through glass tubing fitted into the stopper of the sample flask.

The adsorption of carbon-14-tagged stearic acid as described in previous reports, modified by the described changes in stirring and plating techniques, was used to determine the surface area of samples of powdered nickel and silica. Their surface areas had previously been determined, by gas adsorption, to be 24 and 98 m²/gm, respectively. A silica sample which had been heated at 110°C for 72 hours before it was weighed for the surface area determination gave no evidence of having adsorbed any stearic acid. It evidently readsobered moisture so fast on contact with air that little surface was left exposed to the stearic
acid solution. Samples of the same silica and of powdered nickel were heated 4 hours in a vacuum oven at 115°C and a vacuum of 26 inches of mercury. The sample bottles were capped upon removal from the oven, cooled in a desiccator containing phosphorus pentoxide, and weighed. Each sample was poured into 10 ml of the tagged stearic acid solution contained in a flask which had been preconditioned in the dry box. The sample weight was obtained by difference. The surface area value obtained for the silica was 6.3 m²/gm. It appears that, in order for its surface to be properly exposed to the solution, silica must be not only dried but also degassed and transferred to the stearic acid solution without making any contact with the air.

The surface area obtained for the nickel sample was also lower than the gas adsorption value, 8.8 m²/gm as opposed to 24 m²/gm. Factors which could be responsible for this discrepancy and partly responsible for the much greater discrepancy in the silica are (1) impurities in the benzene used to prepare the stearic acid solution, (2) residual moisture in the powder, and (3) loss of benzene by evaporation during the hour-long period of stirring the powder and adsorbate solution. Judging from the adsorption isotherms of these two powders, the stearic acid solution used for these determinations was strong enough to avoid error from concentration effects.

In the immediate future, the nickel powder used in the described experiments will be studied exhaustively. Its surface area will be determined by both gas adsorption and stearic acid adsorption, with increased emphasis on solvent purity and moisture exclusion, to determine the cause of the low values obtained thus far in surface area determinations utilizing radioactive stearic acid.

It is estimated that approximately 50 per cent of the work required for completion of this project has been accomplished.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief, Chemical Sciences Division
During the month of December the surface areas of several different powders--zinc, zinc oxide, nickel, and cupric oxide--were determined by the sorption of stearic acid-1-carbon-14 and also by the conventional BET (nitrogen adsorption) method. The stearic acid value was lower than the BET value in every case except the zinc oxide, for which a value of 4.7 m²/gm was obtained by both methods. The BET values for zinc, nickel, and cupric oxide were 2.3, 16.8, and 4.2, respectively, as compared with values of 0.7, 6.1, and 2.2 obtained by stearic acid sorption.

Some samples were plated with collodion for counting with the gas flow counter. However, since the average deviation of these plates was greater when counted on the gas flow counter than when counted with a thin end-window geiger tube, collodion plates and the use of the gas flow counter were discontinued.

During January, as many different types of powders as possible will be checked by stearic acid sorption and the BET method. The temperature for stearic acid sorption will be reduced to 60-62° F because the lower tempera-
ture considerably reduces the solubility of stearic acid in benzene, thus reducing the concentration of acid used to maintain the desired $C/C_0$.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief, Chemical Sciences Division
During the month of February the surface areas of several powders---zinc oxide, zinc carbonate, nickel, Linde 5A molecular sieve, silica, Bentonite clay, and ferric oxide---were determined by radioassay of sorbed stearic acid. The technique was the same as that described in Quarterly Report No. 3, but a stearic acid of high purity (Eastman White Label) was substituted for that used previously as the carrier. The stearic acid solutions were made up separately for each sample so that there would be no accumulation of radiation-induced decomposition products such as might possibly occur in stock solutions used over a long period of time.

All of the samples except Bentonite clay were dried in a vacuum oven at 110°C. The clay was dried in a special sample flask, with a stopcock above a ground-glass joint in the neck, that allowed the sample to be simultaneously heated in a Glas-Col heating mantle and degassed with a vacuum pump. The stearic acid solution was then added to the sample, by means of the stopcock, before any air could enter the system.

The surface areas by stearic acid sorption were low for nickel, ferric oxide, and molecular sieve, with values of 6.3, 3.8, and 106 m²/gm, respectively, as opposed to their BET values of 16.8, 10.1, and 688 m²/gm. The low results for molecular sieve were to be expected because of its high porosity. Although its pores, with an average diameter of 5 x 10⁻⁸ cm, are large enough to admit stearic acid molecules, with a diameter of 20.5 x 10⁻¹⁸ cm, the long acid chains can fill the pores and block entrances to them before all the sites on the inner surfaces are filled. Stearic acid sorption values agreed with the BET values for zinc oxide, zinc carbonate, and Bentonite clay, while the stearic acid value for silica, 129 m²/gm, was higher than its BET value of 91 m²/gm.
Since surface areas for all previous clay samples were decidedly lower than the BET values, it appears that it is necessary to exclude air until after the stearic acid solution has been added to the clay.

Plans for the month of March include varying the conditions in surface area determinations of nickel and ferric oxide in order to ascertain the reasons for the consistently low surface area values that have been obtained for these two powders. Also, the annual report will be prepared.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief
Chemical Sciences Division
During this period, experiments have been designed to determine the cause of discrepancies between surface area determinations by the radiostearic acid technique and by the BET nitrogen adsorption method.

Radiostearic acid sorption, as described in Annual Report No. 1, was used to determine the surface area of identical alumina samples having a BET-determined specific surface area of 3.36 square meters per gram. Values for sample I, heated for 3 hours at 110° C, sample II, heated 3 hours in a vacuum oven at 120° C and 25 inches of mercury vacuum, and sample III, which had been heated 3 hours in the BET apparatus at 120° C and a pressure of only 0.1 micron, were 0.95, 1.91, and 1.79 square meters per gram, respectively. These data indicate that heating alumina 3 hours at 110° C and atmospheric pressure does not dry it sufficiently for surface area determinations. The drying methods used for samples II and III seem equally efficient. The discrepancy between samples II and III and the BET value is probably due to the low C/C₀ (equilibrium concentration/saturation concentration) value, 0.12, in these radiostearic acid determinations. The low C/C₀ occurred when the refrigerated water bath became inoperable and the samples intended for 14° C were run at room temperature (23°C). In earlier alumina determinations with C/C₀ values of 1.0 and 0.7, radiostearic acid values were as high as the BET values. A C/C₀ of 0.12 is evidently too low on the sorption isotherm of alumina to give a true surface area.

Three samples of identical zinc sulfide were subjected to different pretreatments before their surface areas were determined by radiostearic acid. Samples were heated (a) overnight at 110° C and atmospheric pressure, (b) one hour in a vacuum oven at 120° C and 29 inches of mercury vacuum, and (c) 5-1/2 hours at 100° C and approximately one millimeter pressure in the sample.
flask with stopcock used for exclusion of air during admission of sorbate solution to the sample. They had specific surface areas of 3.96, 4.0, and 3.5 square meters per gram, respectively. All of these compared favorably with the BET value of 3.7, but the samples were left in contact with the stearic acid solution overnight.

In the immediate future more experiments with zinc sulfide will be conducted with shorter drying times and shorter times of contact between powder and solution to determine the minimum time required for surface area determination.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief, Chemical Sciences Division
During the past month the effects of certain variables on radiostearic acid surface area determinations have been studied. Several determinations utilizing different drying times, drying methods, and powder-solution contact times have been conducted with zinc sulfide, titanium dioxide, and abrasive aluminum oxide powders. Results indicate that zinc sulfide surface areas can be determined simply and quickly with only one hour for equilibration in the stearic acid solution and 2 hours' drying time in an oven at 110° C. Abrasive alumina determinations gave values lower than the BET surface area except when the alumina was vacuum-dried in a sample flask with a stopcock that allows addition of the stearic acid solution without exposure of the dry sample to the atmosphere. In five different experiments with titanium dioxide, including one in which the sample flask mentioned above was used, values of 0.94, 0.87, 0.75, 0.95, and 0.78 square meters per gram were obtained, while the BET value was 2.1. The reason for this discrepancy has yet to be determined.

During this report period, a condensed statement of the work accomplished on the project through April 30, 1960, was prepared for presentation at the Copenhagen Conference by Mr. Hugh Miller.

Additional materials--inert caproic and lauric acids and carbon-14-labelled caproic and lauric acids--have been obtained for future work. They will be used to study the feasibility of porosity determinations utilizing fatty acids of different chain lengths in techniques comparable to surface area determinations by radiostearic acid sorption. If the number of molecules of a short-chain fatty acid sorbed by a powder is significantly greater than
the number of long-chain fatty acid molecules it sorbs, the difference should be due to the presence of pores in the powder.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief, Chemical Sciences Division
Subject: Monthly Progress Letter No. 10, Project No. A-146-3
"An Investigation of the Use of Radioactive Isotopes for Determining the Surface Area of Powdered Materials by Sorption Methods"
Contract No. AT (38-1)-202
Task No. III, Contract Authorization No. IA-59-34
Covering the Period from July 1 to July 31, 1960

During the month of July efforts were directed toward perfecting techniques for surface area determinations that utilize the 12-carbon and 6-carbon saturated acids--lauric and hexanoic acids--so that the usefulness of different length fatty acids in pore size determinations can be ascertained. However, several difficulties were encountered in these experiments.

Because of the high solubility of lauric acid in benzene and other organic solvents (93.6 grams per 100 grams benzene at 20°C), it is necessary to use more concentrated solutions for lauric acid surface area determinations than have been used in stearic acid surface area determinations. A series of tests were made to determine the maximum concentrations that could be plated successfully and the best method of plating them. Solutions as concentrated as 125 grams per liter were plated successfully on chilled Teflon discs. However, because of the hygroscopicity of lauric acid, it was found that they must be stored with a desiccant during transportation to the Radioisotopes Laboratory for counting. Duplicate samples that were allowed to absorb moisture from the atmosphere varied by as much as 20 per cent in counts per minute.

Since hexanoic acid is a liquid at room temperature, from the standpoint of health physics it seems advisable to use its sodium or potassium salt in surface area determinations if a suitable organic solvent can be found. The approximate solubility of sodium and potassium hexanate in several dry organic solvents has been determined. (The general use of aqueous solutions in surface area determinations is not advisable because of the very limited number of powders that do not either sorb water or react with it.) In most cases the solubility is very low. The sodium salt is fairly soluble in methanol, but great care must be taken to dry the solvent, since traces of moisture greatly increase the solubility. The sodium salt of hexanoic acid has more utility.
than its potassium salt because the latter is hygroscopic, while plates of the sodium compound do not appear to change upon exposure to the atmosphere.

Surface area determinations on a high-surface silica (200 square meters per gram by BET) with stearic acid and lauric acid gave values of 55.8 and 161 square meters per gram, respectively. As soon as the technique using hexanoic acid has been perfected, it will be used with the same silica. It appears that the pores of this sample will admit more of the 12-carbon acid than of the 18-carbon acid, and that the surface area value obtained with the 6-carbon acid, hexanoic, should give further indication of the pore size.

Surface area determinations on charcoal (400 square meters per gram by BET) gave very low values by radiostearic acid and radiolauric acid sorption. A different solvent, probably methanol, will be used for future experiments with charcoal; according to the literature, charcoal holds benzene molecules much more strongly than it holds polar molecules such as fatty acids. The similarity of the carbon bonds in charcoal and benzene accounts for the greater attraction between them.

In the immediate future, surface area determinations of powders with methanol solutions of sodium hexanate will be attempted.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief, Chemical Sciences Division
Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 11, Project No. A-446-3
"An Investigation of the Use of Radioactive Isotopes for Determining the Surface Area of Powdered Materials by Sorption Methods"
Contract No. AT (38-1)-202
Task No. III, Contract Authorization No. 1A-59-34
Covering the Period from August 1 to August 31, 1960

Gentlemen:

During the month of August work has been continued on several phases of the project. Because most of the silica samples used in surface area determinations by stearic acid sorption had given values considerably lower than the BET surface area values, more studies of silica were made. Specific surface area determinations by radiostearic acid were made on three different silicas, having BET values of 87.7, 44.4, and 26.6 square meters per gram. Except for sample weights, which were varied in inverse proportion to their BET surface areas, identical conditions were used. The resulting values for specific surface area were 24.4, 13.4, and 7.0 square meters per gram, respectively. Some significance may be attached to the fact that the ratios of BET to stearic acid results for these three samples were fairly close--3.6, 3.3, and 3.8. These figures may indicate that the samples were all porous or that the fatty acid is aligned more parallel to the solid surface than perpendicular to it, thereby occupying a larger area per sorbed molecule. These same silicas were used in determinations utilizing lauric acid as sorbate instead of stearic acid. The specific surface areas thus obtained were 370, 50, and 211 square meters per gram, respectively. It has not yet been determined why these results were so high, unless error was introduced in the dilution factor. (The undiluted solution was too concentrated to plate directly.)

Also, a sorption isotherm for the sorption of stearic acid from benzene solution by silica was determined. Samples of a silica with a BET specific surface area of 26.6 square meters per gram were used with radiostearic acid of several different concentrations. A plot of surface area versus C/C° (equilibrium concentration/saturation concentration) was made and indicated that only over a short range of C/C° does stearic acid sorption give a good
value for the surface area of silica. As in other experiments with silica and stearic acid, the surface area values were lower than the BET values, even when the C/C° was as high as 7.3.

In preparation for surface area determinations with sodium hexanate with the possibility of estimating pore sizes by comparing the sorption of fatty acids (or their salts) of different chain lengths, the exact solubility of sodium hexanate in dry methanol at 14° and 15° C was determined. This salt was then used, at a concentration of 3 grams per 50 ml of methanol solution tagged with 70 microcuries of the carbon-14-labelled hexanate, to determine the surface areas of two high-surface powders for which stearic acid had previously given low surface area values. The conditions of handling, drying, temperature, etc., were the same as those used in experiments utilizing stearic and lauric acids. As a result of preliminary tests, however, the plating technique was changed to the use of aluminum planchets at room temperature. (Refinement of the plating technique is still needed, as the precision was very poor in these determinations.) A carbon black sample with a BET value of 400 square meters per gram had a specific surface area by hexanate sorption of 14 square meters per gram, and for a silica sample the values by the BET method and by hexanate sorption were 200 and 39 square meters per gram, respectively.

Further study of literature pertaining to pore size determinations and to the theoretical aspects of liquid-phase sorption has revealed interesting work pertinent to this investigation. For example, the polar end of the fatty acid chain is usually considered attached to the substrate in monolayer formation, with the other end extending out almost perpendicular to the substrate. However, according to Gasser and Kipling (J. Phys. Chem. 64, 710-15, 1960) straight chain fatty acids in monolayers on a nonpolar material such as charcoal are not attached with their chains perpendicular to the powder surface but, rather, lie parallel to the surface.

In the immediate future, the plating technique for sodium hexanate must be improved. Further surface area determinations with this material and with lauric acid will then be made. In addition, a compound of the same family but even shorter in length—sodium acetate—will be used in these series of determinations aimed at estimation of pore size of powders.

Respectfully submitted,

Margaret C. Kordecki
Project Director
U. S. Atomic Energy Commission  
1717 H. Street, N. W.  
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director  
Office of Isotopes Development

Subject: Monthly Progress Letter No. 12, Project No. A-446-3  
"An Investigation of the Use of Radioactive Isotopes  
for Determining the Surface Area of Powdered Materials  
by Sorption Methods"  
Contract No. AT (38-1)-202  
Task No. III, Contract Authorization No. 1A-59-34  
Covering the Period from October 1 to October 31, 1960

Gentlemen:

During the month of October surface area determinations, by radioassay  
of fatty acid sorption, were attempted with carbon-14-labelled stearic, lauric,  
and hexanoic acids, sodium hexanate, and sodium acetate. The powders used  
were calcium sulfate, zinc oxide, and several different silicas. Both benzene  
and methanol were used as solvents.

A silica with a BET value of 208 square meters per gram was run with  
methanol solutions of lauric acid and sodium hexanate that gave specific  
surface areas of 119 and 29 square meters per gram, respectively. This experi- 
ment indicated that the attraction of methanol to silica may be stronger than  
the attraction of sodium hexanate to silica. A solution of sodium hexanate in  
benzene was also used with a silica sample. The solubility of sodium hexanate  
in benzene is so low that any difference in counts from the original and equili- 
brium solutions was too low to detect with the relatively insensitive counter  
available--an end-window Geiger tube. When the solution was poured off and the  
silica itself was counted, the high count that was obtained indicated that  
sorption of sodium hexanate had occurred, but a count obtained in this way was  
not amenable to surface area calculations.

A solution of hexanoic acid in benzene was prepared and used with two  
silicas having BET surface areas of 87.7 and 44.4 square meters per gram.  
Specific surface areas of 92.4 and 36.1, respectively, were obtained from the  
hexanoic acid sorption. Great difficulties were encountered in counting ali- 
quots of this solution, since hexanoic acid is itself a liquid of fairly high  
vapor pressure. Also, its reaction with strong bases is not fast enough to  
be utilized in plating the acid as a solid salt.
Zinc oxide and calcium sulfate samples were run with methanol solutions of sodium acetate. In both instances no sorption of the radioactive material occurred. While acetic acid would possibly be sorbed by these powders, the problem of plating and counting a volatile liquid would again be met. The use of the carbon-14-tagged liquid acids would be feasible if a liquid scintillation counter were used, but there is not one on the campus and funds are not available for the purchase of one.

During November, methanol solutions of stearic acid will be used with zinc oxide, calcium sulfate, and silica samples. It is necessary to determine whether or not methanol is strongly attracted to these solids and competes with fatty acids for the available surface as it appeared to do in experiments with sodium salts of hexanoic and acetic acids.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief, Chemical Sciences Division
During the month of November several specific surface area determinations by radiostearic acid sorption were run with methanol instead of benzene as solvent. The purpose of these tests was to determine whether very low results (often as low as zero surface area) obtained with lauric acid and several shorter acids in methanol solutions might be due to the preferential sorption of methanol by powder samples. Sorption of stearic acid from methanol gave good results (that is, comparable to the BET values) with zinc powder and zinc oxide, but was ineffective in the case of calcium sulfate. Apparently methanol is not universally appropriate for fatty acid sorption studies.

The use of radioassay for determining the sorption of the shorter, liquid acids appears to be impractical so long as an end-window Geiger counter is used for the assay. Because of the great solubility of these acids in many solvents, they must be used at relatively high concentrations for specific surface area and/or pore size determinations. The changes in concentration due to sorption are then often no greater than the large experimental error incurred when the solutions are plated for radioassay. Consequently, titration with standard base has been used for several tests comparing the sorption, by a porous carbon black, of hexanoic, acetic, and formic acids from aqueous and from methanolic solutions. None of these experiments has yet produced a specific surface area value approaching the sample's BET value of 400 square meters per gram. The concentration at which maximum sorption of each of these acids is found must be determined experimentally. At these concentrations, then, sorption of one or more of these acids may approach the BET value.

During December sorption isotherms will be determined for hexanoic, acetic, and formic acids sorbed by carbon black from methanolic and aqueous
solutions (since benzene adheres to carbon) and sorbed by silica from benzene solutions (since water and methanol adhere to silica). The concentration changes will be determined by titration with standard base. In addition, the sorption of lauric acid-1-carbon-14 from methanol by carbon black and by several different powders will be studied.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief, Chemical Sciences Division
Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 14, Project No. A-446-3
"An Investigation of the Use of Radioactive Isotopes
for Determining the Surface Area of Powdered Materials
by Sorption Methods"
Contract No. AT (38-1)-202
Task No. III, Contract Authorization No. 1A-59-34
Covering the Period from January 1 to January 31, 1961

Gentlemen:

During the month of January, experimental data were obtained for the
sorption isotherm of formic acid sorbed from benzene solutions by a high-
surface silica (193 square meters per gram by BET nitrogen adsorption tech-
nique). The resulting isotherm shows multilayer sorption of formic acid
by silica (see the drawing below). Additional points were also

![Drawing of isotherm](image)

obtained on the isotherm begun previously for acetic acid sorbed from benzene
by the same high-surface silica. The latter isotherm is of a conventional
monolayer type and gives a specific surface area value of 165, which is close
to the BET value for this sample. The sorption of both formic and acetic
acids was determined by titration with standard base.

In addition, the specific surface area of this silica was determined by
the radiostearic acid method described in earlier reports. The value thus
obtained was 41 square meters per gram. A similar determination with radio-
lauric acid gave a value of 69 square meters per gram for this silica.
results, along with the 90 square meters per gram obtained previously from the hexanoic acid isotherm indicate that the sorption of aliphatic, or fatty, acids by high-surface silica does vary, decreasing with increasing chain length of the acid.

In the immediate future, tests will be made to determine whether or not this silica is as highly porous as seems indicated by its sorption of different homologous acids. Further isotherms are also to be determined for the porous carbon black mentioned in the last quarterly report.

Respectfully submitted,

[Signature]

Margaret C. Kordecki
Project Director

Approved:

[Signature]

Fred Sicilio
Co-Technical Director

[Signature]

Richard C. Palmer
Co-Technical Director

[Signature]

Wyatt C. Whitley
Co-Technical and Chief, Chemical Sciences Division
During the past month additional information has been obtained about a silica sample having a BET surface area of 193 square meters per gram. This particular silica has been mentioned in earlier reports describing its sorption of formic, acetic, hexanoic, lauric, and stearic acids. Its true density, determined by measuring the volume of helium gas contained by a sample flask before and after it had been partially filled with a weighed, degassed sample of the silica, was found to be 2.7 grams per cubic centimeter.

Its particle size distribution was determined by means of an optical microscope, and a mean diameter of about 2 microns was found. This value will be checked by measuring particles shown on electron micrographs now being prepared in the electron microscopy laboratory. If the value of 2 microns is approximately correct, a high degree of porosity is indicated by the surface area value of 193, since the specific surface area calculated for nonporous particles of this size with a density of 2.7 is only 1.1 square meters per gram. (A mean diameter of 0.0114 micron would be required to give a surface area of 193.)

In addition, the sorption of carbon-14-labeled lauric acid by this silica was determined again because of the wide deviations obtained in replicate plate counts during previous determinations. The specific surface area available to the lauric acid was found to be 82 square meters per gram, but again the accuracy of the determination was poor because of the plating difficulties.

An article entitled "Surface Area Measurement by the Sorption of Stearic Acid-1-Carbon-14" has also been prepared and submitted to the International Journal of Applied Radiation and Isotopes. Also, a proposal requesting extension of this project for another 12 months was prepared.
During March a rough draft of the annual report will be prepared.

Respectfully submitted,

Margaret C. Kordecki
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief
Chemical Sciences Division
AN INVESTIGATION OF THE USE OF RADIOACTIVE ISOTOPES FOR DETERMINING THE SURFACE AREA OF POWDERED MATERIALS BY SORPTION METHODS

By
MARGARET C. KORDECKI AND MIRIAM L. BARNES

COVERING THE PERIOD
1 APRIL to 31 JULY 1959
Printed 10 August 1959

CONTRACT NO. AT(38-1)-202
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SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPE DEVELOPMENT
GERMANTOWN, MARYLAND

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia
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OFFICE OF ISOTOPE DEVELOPMENT
GERMANTOWN, MARYLAND
ABSTRACT

The use of radioactive stearic acid in benzene solution as a means of accurate surface area measurements of low-surface materials is being investigated. Stearic acid containing 0.4 per cent radiostearic acid (tagged with carbon-14) has been used to determine the range of sample weight, solution concentration and volume, and specific activity that would produce utilizable data. A clay sample with a known surface area of 8 square meters per gram was used in all of the tests. Values of 7.3, 4.5, and 2.7 square meters per gram, respectively, were obtained from samples of one, two, and four grams in 10 ml of 0.001 molar stearic acid (specific activity, 0.2 microcurie per milliliter). As the discrepancy in these results seemed largely due to non-uniform deposits resulting when solution aliquots were transferred to plates and evaporated prior to counting, work has been concentrated on improving the plating technique. Automatic micropipettes were obtained to insure duplication of volumes, and several materials were tested as plates. Of glass, aluminum, Teflon, and tissue paper plates, Teflon gave the most promising results.
TABLE OF CONTENTS

| I. INTRODUCTION | 1 |
| II. EXPERIMENTAL WORK | 2 |
| A. Apparatus | 2 |
| B. Surface Area Determinations | 2 |
| C. Sample-Plating Techniques | 3 |
| III. DISCUSSION AND CONCLUSIONS | 6 |
| IV. FUTURE PROGRAM | 7 |
I. INTRODUCTION

This report summarizes the work performed from April 1 to July 31, 1959. The purpose of the work under this contract is to investigate the use of radioactive tracer atoms in fatty acids or stearates in liquid solution as a means of making accurate surface area measurements of low-surface materials. The determination of surface areas of powdered samples by the sorption of straight-chain fatty acids from liquid solutions is an established technique.\(^1\) The method depends upon the fact that fatty acids, when the affinity of their carboxyl group for the solid is greater than that of the solvent for the solid, form a unimolecular layer of molecules on the solid surfaces. In the past, concentrations of the fatty acid solutions have been determined by conductometric titrations, colorimetric methods, use of a surface balance or surface tension balance, and evaporation of an aliquot to dryness followed by weighing. None of these methods has been entirely satisfactory for both speed and accuracy. Use of a radioactive atom in the fatty acid not only should permit more rapid determination of concentration by electronic methods, but could also increase the accuracy of the determinations to such an extent that much smaller surface areas, such as that of a single crystal, could be measured.

Margaret C. Kordecki is the project director, and Miriam L. Barnes serves in the capacity of research assistant.

II. EXPERIMENTAL

A. Apparatus

As the powdered samples and the stearic acid solutions used for surface-area determinations must be moisture-free, a gloved dry box with an air lock on the side for insertion and removal of materials was obtained. All handling of the materials is done inside this dry box, except the centrifugation. For this step, stoppered centrifuge tubes are employed to avoid contamination by the moisture of the air. An Adams centrifuge is used at speeds greater than 500 RPM.

Small aliquots of the radioactive solutions are plated on glass slides, evaporated, and counted by means of a thin end-window Geiger tube (200 N B) and scaler (Nuclear-Chicago, Model 161 A).

B. Surface Area Determinations

Several experiments have been conducted to determine the optimum solution concentrations and sample weights for use in determining surface areas of powders by means of carbon-14-tagged stearic acid. In these experiments, sample weights of one to four grams in 10 ml. of 0.001 molar stearic acid (in benzene) were used successfully. (Smaller sample weights can be used with correspondingly smaller volumes of stearic acid solution.) The specific activity of this solution of stearic acid was 0.2 microcuries per milliliter, and the radiostearic acid comprised only 0.4 per cent of the total stearic acid.

In all of the experiments thus far, a type of clay with a surface area of approximately 8 m²/gm (determined previously by gas-adsorption methods) was used. Samples of the clay were dried at 110° C, weighed, and placed in the dry box. Inside the dry box each sample was stirred in 10
milliliters of stearic acid solution and allowed to sit 30 minutes or longer before it was centrifuged. Small aliquots (0.05 - 0.15 ml) of the supernatant liquor were transferred to small glass plates and allowed to dry. The plated samples were placed in aluminum planchets and counted with an end-window Geiger tube. Aliquots of the original stearic acid solution were also plated and counted. The surface area of the powder was calculated from the equation shown below.

Specific surface area = 

\[
6.023 \times 10^{-23} \times 20.5 \times 10^{-20} \text{ m}^2 \times \frac{\text{moles of stearic acid adsorbed}}{\text{weight of powder sample}}
\]

Several different values, from 2.7 to 7.3 m²/gm, were obtained for this clay. Experimental data are presented in Table I.

**TABLE I**

SAMPLE COUNTS FOR SURFACE AREA DETERMINATIONS

<table>
<thead>
<tr>
<th>Weight of Powder (gm)</th>
<th>Vol. of Aliquots (ml)</th>
<th>Original Stearic Acid Solution (counts/min)²</th>
<th>Stearic Acid Solution after Contact with Powder (counts/min)²</th>
<th>Surface Area (m²/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2183</td>
<td>0.06</td>
<td>1542 ± 24</td>
<td>127 ± 8</td>
<td>2.7</td>
</tr>
<tr>
<td>2.0645</td>
<td>0.05</td>
<td>968 ± 19</td>
<td>235 ± 10</td>
<td>4.5</td>
</tr>
<tr>
<td>1.0251</td>
<td>0.05</td>
<td>1662 ± 25</td>
<td>646 ± 15</td>
<td>7.3</td>
</tr>
</tbody>
</table>

*Average of two counts

C. Sample-Plating Techniques

Since the discrepancy in the surface-area values obtained in experiments described above seemed largely due to non-uniform deposits of
the plated material, a considerable amount of work has been directed toward perfection of plating techniques. Small aliquots of the 0.001 molar stearic acid in benzene were transferred by hypodermic needle to several different materials, e.g. glass slides, aluminum pans, discs of Teflon sheet (1/16 inch thick), and tissue paper discs. In some instances the aluminum was heated before the solution was placed on it. In other cases, small aluminum rings were placed on top of glass slides and heat was applied from above with an infrared lamp. Also, drops of collodion (in acetone) were placed on some plates before addition of the sample drops. The counts obtained from some of these tests are presented in Table II.

### Table II

<table>
<thead>
<tr>
<th>Plate Material</th>
<th>Aliquot Volume (ml)</th>
<th>Counts/Min</th>
<th>Counts/Min/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon</td>
<td>.2</td>
<td>4951 ± 42</td>
<td>24755 ± 210</td>
</tr>
<tr>
<td>Teflon</td>
<td>.2</td>
<td>5000 ± 42</td>
<td>25000 ± 210</td>
</tr>
<tr>
<td>Teflon</td>
<td>.2</td>
<td>5702 ± 44</td>
<td>28510 ± 220</td>
</tr>
<tr>
<td>Teflon</td>
<td>.2</td>
<td>5029 ± 42</td>
<td>25145 ± 210</td>
</tr>
<tr>
<td>Teflon</td>
<td>.05</td>
<td>1609 ± 24</td>
<td>32180 ± 480</td>
</tr>
<tr>
<td>Teflon</td>
<td>.05</td>
<td>1562 ± 24</td>
<td>31240 ± 480</td>
</tr>
<tr>
<td>Teflon</td>
<td>.1</td>
<td>2662 ± 33</td>
<td>26620 ± 330</td>
</tr>
<tr>
<td>Teflon</td>
<td>.1</td>
<td>2390 ± 31</td>
<td>23900 ± 310</td>
</tr>
<tr>
<td>Tissue Paper</td>
<td>.05</td>
<td>1018 ± 20</td>
<td>20380 ± 400</td>
</tr>
</tbody>
</table>

(Continued)
TABLE II (Continued)

COUNTS OF BETA RADIATION FROM PLATED ALIQUOTS OF STEARIC ACID CONTAINING 0.4 PER CENT RADIOSTEARIC ACID

<table>
<thead>
<tr>
<th>Plate Material</th>
<th>Aliquot Volume (ml)</th>
<th>Counts/Min</th>
<th>Counts/Min/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tissue Paper</td>
<td>0.05</td>
<td>1000 ± 19</td>
<td>20000 ± 380</td>
</tr>
<tr>
<td>Tissue Paper</td>
<td>0.05</td>
<td>1150 ± 21</td>
<td>23000 ± 420</td>
</tr>
<tr>
<td>Tissue Paper</td>
<td>0.05</td>
<td>1100 ± 20</td>
<td>22000 ± 400</td>
</tr>
<tr>
<td>Tissue Paper</td>
<td>0.05</td>
<td>1106 ± 20</td>
<td>22160 ± 400</td>
</tr>
<tr>
<td>Tissue Paper</td>
<td>0.05</td>
<td>1094 ± 20</td>
<td>21880 ± 400</td>
</tr>
</tbody>
</table>
III. DISCUSSION AND CONCLUSIONS

Preliminary experiments with a clay having a surface area of 8 square meters per gram (determined by the gas adsorption method) have given results of the same order of magnitude, 2.7 to 7.3 square meters per gram, but much better agreement between duplicate samples is necessary. There were two probable sources of error which account for the discrepancy in these values. One was the variation in aliquot volume due to the difficulty of controlling pipette delivery while wearing the rubber gloves attached to the dry box. Automatic micropipettes have been purchased and should solve this difficulty.

The second, and perhaps major, source of error was the non-uniform deposit formed on the plate as the benzene evaporated. Some areas of the stearic acid deposit were thick enough to absorb a significant amount of the low-energy beta radiation emitted by carbon-14. In addition, the radii of these deposits varied so that some portions of them may have been out of range of the Geiger tube.

Of the various materials which have been used in plating these samples, Teflon sheet seems to be the most promising. Of four 0.2-ml samples plated on Teflon, three were within one per cent of their mean value. Smaller aliquots, precisely measured with automatic micropipettes, will be more desirable, however, to avoid the possibility of self-adsorption of radiation by the heavier deposits. If the plating technique can be developed to give consistently good duplicate values (within one per cent of each other), continued use of an end-window Geiger tube for counting samples will be adequate. Otherwise, a gas-flow counter may be required to obtain the desired accuracy.
IV. FUTURE PROGRAM

In the immediate future, work will be continued to develop a plating technique that will consistently give uniform deposits with minimum self-adsorption of radiation. When the plating technique has been perfected, the entire procedure will be standardized for several different sample weights. Also, various materials with surface areas from 0.5 to 50 square meters per gram will be used to determine the limits of the applicability of the fatty acid sorption method.

Respectfully submitted:

Margaret C. Kordecki
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division
AN INVESTIGATION OF THE USE OF RADIOACTIVE ISOTOPES FOR DETERMINING THE SURFACE AREA OF POWDERED MATERIALS BY SORPTION METHODS

By

MARGARET C. KORDECKI AND MIRIAM B. GANDY

COVERING THE PERIOD
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GERMANTOWN, MARYLAND
ABSTRACT

As a result of several surface area determinations on kaolin and of a literature survey on liquid-phase adsorption, the concentration of stearic acid solutions used in these determinations was increased from 2.8 to 17 grams per liter. Adsorption isotherms (plots of surface area versus $C/C_0$, where $C$ is the equilibrium concentration of the solution used and $C_0$ is the saturation concentration) of kaolin--steaeric acid--benzene systems indicate the higher concentration is required to avoid dependence of adsorption on concentration, such as occurs in more dilute solutions.

As plated aliquots of the more concentrated stearic acid were very irregular in size, shape, and density, improvement of plating techniques was required. In a series of tests, aliquots were plated on several different surfaces, such as emery paper, emery cloth, legal paper, lens paper, filter paper, glass, Teflon, 20-micron glass beads glued to a glass surface, aluminum and rubber. Some aliquots were also discharged on watch glasses containing small volumes of various solvents, either as diluents, spreading agents, or support for the stearic acid film. Water, acetone, benzene, nitrobenzene, amyl acetate, and ethylene glycol were used in these tests, with the most uniform deposit forming on top of nitrobenzene. The desired precision in making duplicate plates has not been attained. Since the figure used to calculate surface area, i.e., the difference between the original and equilibrium counts, is usually less than 15 per cent of the original count, an average deviation of 2 per cent or higher in these counts precludes any high degree of accuracy. It also rules out the usefulness of the radioactive tracer technique for kaolins of very low surface area (2 square meters per gram, or less). However, the adsorption isotherms of metallic powders and some other materials indicate that greater accuracy can be expected with them, through the use of more dilute stearic acid solutions.
### TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>iii</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. EXPERIMENTAL WORK</td>
<td>1</td>
</tr>
<tr>
<td>A. Surface Area Determinations</td>
<td>1</td>
</tr>
<tr>
<td>B. Sample-Plating Techniques</td>
<td>1</td>
</tr>
<tr>
<td>III. DISCUSSION AND CONCLUSIONS</td>
<td>3</td>
</tr>
<tr>
<td>IV. FUTURE PROGRAM</td>
<td>6</td>
</tr>
</tbody>
</table>

This Report Contains 6 Pages.
I. INTRODUCTION

This report summarizes the work performed from August 1, 1959, to October 31, 1959. During this quarter a literature survey on liquid-phase adsorption was completed. Also, experimental work was continued with the object of establishing techniques for the use of radioactive tracer atoms in fatty acids or stearates dissolved in nonaqueous liquids as a means of accurate measurement of surface area for materials with relatively small surfaces. Stearic acid tagged with carbon-14 has been used as the tracer in all experimental work thus far. All powders used in surface area determinations during this period were samples of kaolin.

II. EXPERIMENTAL WORK

A. Surface Area Determinations

Samples of two kaolins, one with a surface area of 8 square meters per gram and one with a surface area of 17.3 square meters per gram (determined by the nitrogen-adsorption method), were dried at 110° C and weighed in small, dry flasks with ground glass stoppers. To each flask were added 10 ml of a benzene solution of stearic acid and a small polyethylene-coated stirring rod. The flask was stoppered and put in the dry box, where it was stirred one hour by a magnetic stirrer. The mixture was then centrifuged, and 0.1-ml or 0.05-ml aliquots were transferred to Teflon plates (discs of Teflon 1-1/4 inches in diameter and 1/16 inch thick), allowed to evaporate at room temperature, and counted. Aliquots of the original solution were also plated and counted. Several experiments were conducted with a solution containing 0.28 gram of stearic acid and 0.02 millicurie of stearic acid-1-carbon-14 per 100 ml. The concentration was then increased to 1.7 grams and 0.5 millicurie per 100 ml. Data from the experiments are presented in Table I. It will be noted that only one of these determinations checked with the surface area value determined by nitrogen adsorption. The discrepancies are discussed in Chapter III of this report.

B. Sample-Plating Techniques

A solution of stearic acid in benzene (17 grams per liter) that contained no radioactive tracer was used for many tests of plating techniques. The uniformity of the stearic acid deposits in these tests was estimated visually.
### TABLE I

**THE SURFACE AREA OF KAOLIN SAMPLES**

<table>
<thead>
<tr>
<th>Kaolin Sample Description (S by Nitrogen Adsorption) (M²/Gm)</th>
<th>Stearic Acid Solution</th>
<th>Plating Tool</th>
<th>Original Solution Avg. Count from 3 or More Plates (C/Min)</th>
<th>Original Solution Avg. Deviation in Plates (%)</th>
<th>Solution in Equilibrium with Kaolin Avg. Count from 3 or More Plates (C/Min)</th>
<th>Solution in Equilibrium with Kaolin Avg. Deviation in Plates (%)</th>
<th>S from Stearic Acid Sorption (M²/Gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>A</td>
<td>M</td>
<td>2527</td>
<td>6.6</td>
<td>706</td>
<td>13.4</td>
<td>4.3</td>
</tr>
<tr>
<td>8</td>
<td>A</td>
<td>M</td>
<td>2450</td>
<td>7.1</td>
<td>1583</td>
<td>10.2</td>
<td>4.3</td>
</tr>
<tr>
<td>8</td>
<td>A</td>
<td>H</td>
<td>3392</td>
<td>5.5</td>
<td>2823</td>
<td>2.9</td>
<td>2.0</td>
</tr>
<tr>
<td>8</td>
<td>B</td>
<td>M</td>
<td>17654</td>
<td>4.5</td>
<td>14832</td>
<td>3.4</td>
<td>11.9c</td>
</tr>
<tr>
<td>8</td>
<td>B</td>
<td>M</td>
<td>17656</td>
<td>1.7</td>
<td>13412</td>
<td>3.0</td>
<td>17.9c</td>
</tr>
<tr>
<td>8</td>
<td>B</td>
<td>H</td>
<td>6140</td>
<td>10.4</td>
<td>5871</td>
<td>4.8</td>
<td>3.2e</td>
</tr>
<tr>
<td>17.3</td>
<td>B</td>
<td>M;P</td>
<td>29253</td>
<td>4.6</td>
<td>27305</td>
<td>2.3</td>
<td>18.3</td>
</tr>
</tbody>
</table>

* A = 0.28 gm stearic acid/100 ml of solution and 0.02 millicurie of carbon-14 per 100 ml of solution; B = 1.7 gm stearic acid/100 ml of solution and 0.5 millicurie of carbon-14 per 100 ml of solution.

* M = automatic micropipette; H = hypodermic syringe; P = 0.1-ml pipette.

* These results are from only one experiment in which two series of aliquots were plated, one by automatic micropipette and one by hypodermic needle.

* Plated on discs of legal paper instead of the Teflon discs used in the other experiments on this table.

* Meaningless, as discrepancy in counts from duplicate plates is greater than the difference between 6140 and 5871 counts/min.
Aliquots of this solution (0.1 and 0.05 ml) were plated on fine emery cloth, fine emery paper, legal paper, lens paper, filter paper, Teflon, glass, aluminum, and rubber. In some cases, cells were made by building up a rim of Teflon paint or other material around the edge of glass and Teflon discs or by gluing microscope mounting cells (glass circles 3 mm in height) on glass plates. Other aliquots were discharged onto watch glasses containing various reagents either to dilute the solution or to support the deposit formed as the benzene evaporated. Nitrobenzene, acetone, benzene, water, ethylene glycol, and amyl acetate were among the reagents tested. In these tests, deposits formed on top of 0.1 and 0.05 ml of nitrobenzene were the most uniform in appearance. Other plates were made by smearing epoxy resin on glass plates or cover glasses and then covering the coated surface with 20-micron glass beads. After these plates had been oven-dried, any loose beads were removed, and the plates were ready to receive the sample solution. The tests judged by visual comparison to give the most reproducible deposits of stearic acid were repeated with the radioactive solution of the same concentration. Counts from some of these plates are given in Table II. Plating the solution on a nitrobenzene substrate seems to give good results. Plates prepared by attaching glass beads to glass slides with epoxy resin were satisfactory.

III. DISCUSSION AND CONCLUSIONS

As a result of the completed literature survey and of surface area determinations made in this laboratory, the concentration of stearic acid in benzene solutions used for kaolin surface area determinations was increased by a factor of five. The large increase was found necessary because the adsorption isotherm for a system of kaolin, stearic acid, and benzene\(^1\) indicates a large dependence on concentration in the adsorption of stearic acid by kaolin when the concentration of the solution in equilibrium with the powder is less than about 12 grams per liter. In experiments using the more dilute stearic acid, surface areas of

### TABLE II

**COMPARISON OF PLATING TECHNIQUES**

<table>
<thead>
<tr>
<th>Plate Material</th>
<th>Plating Tool&lt;sup&gt;a&lt;/sup&gt;</th>
<th>No. of Plates</th>
<th>Avg. Count (C/Min)</th>
<th>Avg. Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon</td>
<td>M</td>
<td>5</td>
<td>2322</td>
<td>4.0</td>
</tr>
<tr>
<td>Teflon</td>
<td>M</td>
<td>4</td>
<td>2178</td>
<td>6.9</td>
</tr>
<tr>
<td>Teflon with plastic rim</td>
<td>M</td>
<td>4</td>
<td>3576</td>
<td>7.0</td>
</tr>
<tr>
<td>Filter paper</td>
<td>M</td>
<td>4</td>
<td>15299</td>
<td>5.0</td>
</tr>
<tr>
<td>Lens paper</td>
<td>M</td>
<td>3</td>
<td>7580</td>
<td>4.0</td>
</tr>
<tr>
<td>Emery cloth</td>
<td>H</td>
<td>4</td>
<td>4682</td>
<td>5.0</td>
</tr>
<tr>
<td>Teflon</td>
<td>H</td>
<td>4</td>
<td>26948</td>
<td>4.9</td>
</tr>
<tr>
<td>Wet filter paper</td>
<td>M</td>
<td>6</td>
<td>2139</td>
<td>9.2</td>
</tr>
<tr>
<td>1:1 benzene and nitrobenzene in watch glass</td>
<td>H</td>
<td>4</td>
<td>1653</td>
<td>6.7</td>
</tr>
<tr>
<td>Glass beads on glass plate</td>
<td>P</td>
<td>2</td>
<td>542</td>
<td>3.5</td>
</tr>
<tr>
<td>Glass beads on glass plate</td>
<td>P</td>
<td>3</td>
<td>723</td>
<td>4.8</td>
</tr>
<tr>
<td>Glass beads on glass plate</td>
<td>P</td>
<td>2</td>
<td>437</td>
<td>0.5</td>
</tr>
<tr>
<td>Glass beads on glass plate</td>
<td>P</td>
<td>2</td>
<td>352</td>
<td>13.5</td>
</tr>
<tr>
<td>Teflon</td>
<td>P</td>
<td>3</td>
<td>2126</td>
<td>4.5</td>
</tr>
<tr>
<td>Wet filter paper</td>
<td>M</td>
<td>4</td>
<td>27349</td>
<td>4.4</td>
</tr>
<tr>
<td>Nitrobenzene on watch glass</td>
<td>M</td>
<td>3</td>
<td>25072</td>
<td>1.1</td>
</tr>
<tr>
<td>Nitrobenzene on watch glass</td>
<td>P</td>
<td>2</td>
<td>29589</td>
<td>2.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>M = automatic micropipette; H = hypodermic syringe; P = 0.1-ml pipette.
kaolin were consistently lower than the values obtained by nitrogen adsorption. The usual form of the adsorption isotherm is a plot of either the surface area of the powder or the acid adsorbed per gram of powder versus $C/C_0$, where $C$ is the equilibrium concentration and $C_0$ is the concentration of a saturated solution (44.6 grams per liter for stearic acid in benzene at 70°C). In the case discussed here, this curve becomes a straight line parallel to the x-axis at a value of 0.3 for $C/C_0$, and any value as high as or higher than 0.3 may be selected for the stearic acid solutions used to determine the surface area of kaolin. However, when the stearic acid analysis is accomplished by using radioactive stearic acid as a tracer, the $C/C_0$ value should not exceed 0.3 by any significant amount because the difference in counts for the solution before and after its contact with the adsorbent, which is the measure of the stearic acid adsorbed, becomes smaller in proportion to the total counts, thus decreasing the reliability of the analysis.

Difficulties in preparing duplicate plates from benzene solutions of stearic acid have been magnified by the use of more concentrated solutions. The wide variations in size, shape, and thickness of deposits have caused some self-adsorption of the beta radiation and large average deviations in counts from duplicate plates (from 2 to 13 per cent). Consequently, during the latter part of the quarter experimental efforts were again concentrated on improving plating techniques. Rough surfaces such as emery cloth, emery paper, and glass beads glued on glass plates were used with the expectation that the particles would seed the solution as the benzene evaporated, thus preventing the build-up, which has been evident in some cases, of a thick rim of stearic acid at the periphery of the deposit. Plates of emery cloth and emery paper were unsatisfactory because they adsorbed a large portion of the solution. The glass slides coated with glass beads gave very good results when the glass bead coatings were identical in size, depth, etc. The usefulness of the glass bead slide seems to be limited only by the difficulty of preparing identical deposits of glass beads on glass surfaces. These slides can be reused after having been washed with benzene (the epoxy resin used to glue the beads to the glass slide is not soluble in benzene), so preparation of a relatively few would be required.
In some cases, the use of a liquid substrate in a watch glass on which the stearic acid was plated improved the uniformity of the film remaining when the benzene had evaporated. The greatest uniformity was found when the substrate was nitrobenzene, apparently because its surface tension is significantly higher than that of benzene and at the same time it is miscible with benzene.

At the present time the accuracy of surface area determinations of kaolin by adsorption of radioactive stearic acid is considerably below the desired level, primarily because small differences between the relatively high concentrations of the original and equilibrium solutions cannot be measured with the desired precision (one per cent average deviation). The accuracy will be better for samples with larger surface areas, e.g. 40 to 50 square meters per gram, and can be improved by using larger powder samples, up to the limit (about 4 grams in 10 ml) imposed by the problem of mixing as the proportion of powder to liquid is increased. Surface areas of some materials, e.g. metallic powders, should be obtainable with much better accuracy because their adsorption isotherms allow the use of more dilute stearic acid solutions.

IV. FUTURE PROGRAM

In the immediate future, surface area determinations by adsorption of stearic acid will be run on powdered nickel and on silica. As these materials have straighter adsorption isotherms than does kaolin, a more dilute solution of stearic acid can be used (with $C/C_o$ as low as 0.05), and a resultant increase in accuracy is anticipated. Also, some exploratory work will be done to determine the practicality of counting the radioactive adsorbate on the powder itself instead of counting the solution before and after its being stirred with the powder.

Respectfully submitted:

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QUARTERLY TECHNICAL STATUS REPORT NO. 3
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AN INVESTIGATION OF THE USE OF RADIOACTIVE ISOTOPES FOR
DETERMINING THE SURFACE AREA OF POWDERED MATERIALS BY
SORPTION METHODS

By
MARGARET C. KORDECKI AND MIRIAM B. GANDY

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Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

Engineering Experiment Station
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AN INVESTIGATION OF THE USE OF RADIOACTIVE ISOTOPES FOR DETERMINING THE SURFACE AREA OF POWDERED MATERIALS BY SORPTION METHODS

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ABSTRACT

The technique developed for surface area determinations by radiostearic acid sorption has been modified by the use of lower temperatures. Because of the considerable drop in stearic acid solubility as the temperature is decreased from 25°C to 15°C, the desired \( \frac{C}{C_0} \) value can be maintained with lower initial concentrations \( (C_i) \) of stearic acid at the lower temperature. Thus the difference in \( C_i \) and \( C \), which is the measure of sorbed acid, becomes larger in relation to \( C_i \) and the accuracy of the measurement is enhanced.

A new method of plating aliquots of stearic acid solutions has been adopted as standard procedure. It consists of pipetting 0.1-ml aliquots to chilled 25-mm watch glasses and allowing the solvent to evaporate slowly in the refrigerator. The average deviation in replicate plates is usually under 2 per cent.

Surface areas of several different samples have been determined by stearic acid sorption and compared with BET surface area values (nitrogen adsorption) obtained for the same powders. Values by the two different methods agreed for glass beads, titanium dioxide, zinc oxide, cupric oxide, and zinc but did not check for silica, iron, nickel, and several different clays.
# Quarterly Technical Status Report No. 3, Project No. A-446-3

**TABLE OF CONTENTS**

| TITLE PAGE | 1 |
| ABSTRACT | 11 |
| TABLE OF CONTENTS | iii |
| I. INTRODUCTION | 1 |
| II. EXPERIMENTAL WORK | 1 |
| A. Surface Area Determinations | 1 |
| B. Plating Techniques | 3 |
| III. DISCUSSION AND CONCLUSIONS | 4 |
| IV. FUTURE PROGRAM | 5 |

This Report Contains 6 Pages.
I. INTRODUCTION

This report summarizes the work performed from November 1, 1959, to January 31, 1960. The purpose of the work under this contract is to investigate the use of radioactive tracer atoms in fatty acids or stearates in liquid solution as a means of making accurate surface area measurements of low-surface materials. During this quarter experimental work was continued on techniques for the use of carbon-14 tracer atoms in stearic acid as a means of accurate measurement of surface area for powders with small or intermediate range surface areas. The surface areas of nickel, silica, cupric oxide, zinc, zinc oxide, titanium dioxide, glass beads, iron, and several clays were determined by radioassay of the stearic acid removed from benzene solutions by the powder samples. The values thus obtained were compared with the specific surface area values which had previously been determined for these samples by the conventional BET (nitrogen adsorption) method.

II. EXPERIMENTAL

A. Surface Area Determinations

The procedure developed during the preceding quarter for surface area determinations by sorption of stearic acid-1-carbon-14 has been somewhat modified. After the original stearic acid solution (its concentration shall be designated as C₁) has been added to the flask containing the dry powder sample, the system is allowed to equilibrate for one hour, with occasional shaking, in a controlled temperature bath maintained below room temperature, e.g. at 15°C. The solution is then centrifuged briefly, and, to avoid desorption by powder remaining in the centrifuge tube, the supernatant liquid (concentration = C; saturation concentration = C₀) is poured into another flask which is stoppered and allowed to reach room temperature before four or more aliquots are plated. (Plating at the lower temperature was not desirable because it gave more opportunity for contamination of work bench, refrigerated water bath, etc., with the radioactive material.)

Standard BET determinations of surface area by nitrogen adsorption had been run previously on all the samples used in the stearic acid sorption experiments. However, some of the BET determinations were repeated to ascertain whether or not the surface areas of these powders had changed with ageing
on the shelf for long periods of time (as long as 2 or 3 years in some instances). New BET values for samples of cupric oxide, nickel, zinc oxide, and zinc were 4.2, 16.8, 4.7, and 2.3, respectively, and were essentially the same as the original values. Of all the surface area determinations made by radioassay of stearic acid during this quarter, those for titanium dioxide, glass beads, zinc oxide, cupric oxide, and zinc samples agreed with the BET values, while those for silica, iron powder, several types of clays, and nickel did not check the BET values. The experimental data are presented in Table I.

### Table I

**Specific Surface Area (S_w) Determinations**

<table>
<thead>
<tr>
<th>Sample Powder</th>
<th>S_w by BET (M^2/Gm)</th>
<th>Temperature (°C)</th>
<th>C/C_o^a</th>
<th>C_i^b (Gm/Liter)</th>
<th>S_w (M^2/Gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-5</td>
<td>2.2</td>
<td>15.6</td>
<td>.6</td>
<td>8.15</td>
<td>2.2</td>
</tr>
<tr>
<td>Ala. fire clay</td>
<td>13.4</td>
<td>15.6</td>
<td>.6</td>
<td>8.15</td>
<td>15.6</td>
</tr>
<tr>
<td>Bentonite clay</td>
<td>15</td>
<td>15.6</td>
<td>.6</td>
<td>8.15</td>
<td>6.5</td>
</tr>
<tr>
<td>Cupric oxide</td>
<td>4.2</td>
<td>16.7</td>
<td>.8</td>
<td>10.79</td>
<td>3.0</td>
</tr>
<tr>
<td>Iron powder</td>
<td>21.3</td>
<td>14</td>
<td>.8</td>
<td>3.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Glass beads</td>
<td>0.4</td>
<td>14</td>
<td>.5</td>
<td>3.43</td>
<td>0.6</td>
</tr>
<tr>
<td>Kaolin 788</td>
<td>18.5</td>
<td>15.6</td>
<td>.6</td>
<td>8.15</td>
<td>4.8</td>
</tr>
<tr>
<td>Nickel powder</td>
<td>16.8</td>
<td>22</td>
<td>.2</td>
<td>8.6</td>
<td>8.8</td>
</tr>
<tr>
<td>Silica</td>
<td>98</td>
<td>22</td>
<td>.2</td>
<td>8.6</td>
<td>38</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>7.7</td>
<td>14</td>
<td>.5</td>
<td>3.43</td>
<td>5.6</td>
</tr>
<tr>
<td>Vollander clay</td>
<td>24</td>
<td>14</td>
<td>.3</td>
<td>3.0</td>
<td>7.8</td>
</tr>
<tr>
<td>Zinc</td>
<td>2.3</td>
<td>22</td>
<td>.3</td>
<td>10.79</td>
<td>1.2</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>4.7</td>
<td>22</td>
<td>.3</td>
<td>10.79</td>
<td>4.7</td>
</tr>
</tbody>
</table>

^aC = concentration of stearic acid solution in equilibrium with sorbent; C_o = concentration of saturated solution at the appropriate temperature.

^bC_i = initial concentration of stearic acid-benzene solution.
B. Plating Techniques

The plating technique which has now been adopted for standard procedure consists of pipetting 0.1-ml aliquots to 25-mm watch glasses which have been chilled in a refrigerator. The watch glasses are kept cold on a bed of cracked ice during the plating process and are then returned to the refrigerator for slow evaporation of the solvent. The average deviation in these plates is usually under 2 per cent.

In addition, a standard curve has been constructed to correct for the increase in self-adsorption of radiation which occurs with increasing concentration in plated samples. A standard solution containing 0.815 gram of stearic acid and 0.20 mc of carbon-14 per 100 ml of solution was diluted to give five additional concentrations containing the same ratio of radioactive stearic acid to carrier stearic acid. Four aliquots of each of these solutions were plated in the manner described above. The average count per minute for each concentration was plotted versus concentration. After 0.1-ml plates of unknown solutions having the same ratio of tagged stearic acid to carrier (0.245 mc/gm) have been counted, their concentrations can be read directly from the curve. (The effect of tube deadtime is also taken care of by these plots.) The only additional correction needed is to adjust the count for tube response as indicated by counting a carbon-14 standard source whenever sample plates are counted. Data from this experiment are given in Table II.

### TABLE II

EFFECTS OF SELF-ADSORPTION AND TUBE DEADTIME SHOWN BY COUNTS OF STANDARD SOLUTIONS

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>Concentration (Gm/Liter)</th>
<th>Radiation Counts (Counts/Min)</th>
<th>Average Deviation in Four Plates (%)</th>
<th>Standard Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.15</td>
<td>14,642 ± 70</td>
<td>2.3</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>6.52</td>
<td>11,742 ± 60</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>5.21</td>
<td>9,920 ± 58</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>3.26</td>
<td>6,190 ± 46</td>
<td>0.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>2.60</td>
<td>5,101 ± 41</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>6</td>
<td>1.30</td>
<td>2,640 ± 30</td>
<td>2.1</td>
<td>2.9</td>
</tr>
</tbody>
</table>

(Continued)
TABLE II (Continued)

EFFECTS OF SELF-ADSORPTION AND TUBE DEADTIME SHOWN 
BY COUNTS OF STANDARD SOLUTIONS

<table>
<thead>
<tr>
<th>Alcohols of 0.1 ml plated on chilled 25-mm watch glasses.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only three plates. One was ruined before counting.</td>
</tr>
</tbody>
</table>

III. DISCUSSION AND CONCLUSIONS

The lower temperature now used in the radiostearic acid determinations of surface area enhances their accuracy because of the sharp decrease in solubility of stearic acid in benzene as the temperature is lowered (from 12.4 gm/100 gm benzene at 30°C to 0.24 gm/100 gm benzene at 10°C). Since at lower temperatures a lower initial concentration, $C_i$, is required to give the desired $C/C_0$ value (0.3 or higher in the case of kaolin and titanium dioxide), the difference between $C_i$ and $C$, which is the measure of sorbed stearic acid, becomes greater in proportion to $C_i$ and $C$. Thus one difficulty encountered earlier in the project appears to be solved, viz., differences between average counts for $C_i$ and $C$ which often were no higher than average deviations in the counts for replicate plates of $C_i$.

It is not to be expected that specific surface area values by the BET method and by the radiostearic acid technique will check exactly. The BET values may be as much as 15 per cent inaccurate in the lower range of surface areas ($< 10 \text{ m}^2/\text{gm}$). Thus values of 7.7 by BET and 5.6 by radiostearic acid, as in the case of titanium dioxide (see Table I), are considered to agree.

However, wide discrepancies between values obtained by the two types of determinations have been found in several cases, notably clays, nickel, and silica. As yet it is not known whether the variance is due to preferential sorption of impurities which might be present in the original stearic acid, to the pore size of the powdered materials, or to some facet of the experimental technique such as exposure to moisture in the air as the samples are removed from the vacuum oven. In addition, there is some possibility of new impurities being continuously produced in stock solutions of the radiostearic
acid by decomposition of the acid in the presence of ionizing radiation. It has been shown that high energy radiations decompose long chain, saturated fatty acids,¹ and a very small amount of decomposition of stearic acid may be induced by beta radiation from the carbon-14 tracer atoms. Some stock solutions used in this investigation had been stored for periods of 4 or 5 weeks, so there might have been an accumulation of relatively small molecules produced by decomposition of the long stearic acid molecules. These smaller molecules could be preferentially adsorbed by some sorbent powders with a resulting low radioassay of sorbed stearic acid-1-carbon-14.

IV. FUTURE PROGRAM

In the immediate future, samples for which results have been poor will be rerun with a new brand of stearic acid carrier (Eastman White Label) that is claimed to be purer than the material (from Matheson, Coleman & Bell) used up to now. Also, a special sample flask with a three-way stopcock above the stopper will be used. With this flask the sample can be evacuated while it is being dried at 110°C in a Glas-Col heating mantle. The stopcock is then turned to the other outlet where a burette of the stearic acid solution is attached and the solution can be added to the flask without allowing any air to reach the sample. This innovation is expected to result in higher surface area values for samples which tend to pick up moisture from the air very quickly.

In addition, stock solutions of the carrier stearic acid and radiostearic acid will no longer be used. Fresh solutions will be made up for each sample

to avoid the possible accumulation of decomposition products discussed in Chapter III.

Respectfully submitted:

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Approved:

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AN INVESTIGATION OF THE USE OF RADIOACTIVE ISOTOPES FOR DETERMINING THE SURFACE AREA OF POWDERED MATERIALS BY SORPTION METHODS

By

MARGARET C. KORDECKI AND MIRIAM L. GANDY

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QUARTERLY TECHNICAL STATUS REPORT NO. 4
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AN INVESTIGATION OF THE USE OF RADIOACTIVE ISOTOPES FOR
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ABSTRACT

The technique developed in this project for surface area determinations by radiostearic acid sorption has been examined to determine the simplest sample-drying technique, the minimum sample-drying time, and the minimum sorbate-sorbent contact time that would be adequate for most types of powders. Samples of several powders--zinc sulfide, alumina, titania, sodium carbonate, and sodium bicarbonate--were dried by one of the following methods before determination of their surface areas: (1) in an oven at 110° C and atmospheric pressure; (2) in a vacuum oven at 120° C and 100 mm of pressure; and (3) at 100° C and 100 mm of pressure in a sample flask with a stopcock for adding the stearic acid solution without admitting air to the dried sample. Several different drying times were also compared. It was found that an inert powder such as zinc sulfide can be sufficiently dried in 2 hours at 110° C and atmospheric pressure. Basic powders, such as sodium bicarbonate, can react with stearic acid if traces of moisture are present and must be dried at low pressure in the flask designed to exclude air from the dried sample. Materials with a great affinity for water must likewise be dried at reduced pressures and protected from contact with the atmosphere. Experiments designed to compare different times of contact between the dried sample and the stearic acid solution indicated that one hour is sufficient to reach sorption equilibrium, within the limits of experimental error.

In an experiment comparing the sorption of stearic acid, C_{18}H_{36}O_{2}, with the sorption of lauric acid, C_{12}H_{24}O_{2}, on porous charcoal powder (with a BET value of 400 m²/gm), the fatty acid sorption values for surface area were 61.7 and 63.6 m²/gm, respectively. Apparently the shorter acid molecules could not penetrate the pores of the powder any more than could the longer ones.
LIST OF TABLES

I. COMPARISON OF DRYING METHODS, DRYING TIMES, AND SORBENT-SORBATE CONTACT TIMES IN SPECIFIC SURFACE AREA ($S_W$) DETERMINATIONS BY RADIOSTEARIC ACID SORPTION ........................................... 3

II. SPECIFIC SURFACE AREA ($S_W$) DETERMINATIONS BY SORPTION OF STEARIC AND LAURIC ACIDS ON CHARCOAL .................................................... 4
I. INTRODUCTION

This report summarizes the work performed from April 1, 1960, to June 30, 1960. The purpose of the work under this contract is to investigate the use of radioactive tracer atoms in fatty acids or stearates in liquid solution as a means of making accurate surface area measurements of low-surface materials and porosity measurements of porous materials. During this quarter experimental work, utilizing the techniques described in Annual Report No. 1, was concentrated on determining the drying times and techniques adequate for powders before their surface area determinations by radiostearic acid sorption and on determining the time required for powders to reach approximate equilibrium with the sorbate solution.

Also, preparations were made for studying the possibility of porosity measurements by fatty acid sorption. Stock solutions of lauric acid (dodecanoic acid, C_{12}H_{24}O_{2}) and of caproic acid (hexanoic acid, C_{6}H_{12}O_{2}), each tagged with carbon-14, were prepared. These are to be utilized in surface area determinations along with stearic acid (C_{18}H_{36}O_{2}) in the expectation that for nonporous materials the moles of each of these acids sorbed will be approximately the same, while for porous materials the moles of acid sorbed should increase with decreasing length of the acid chain. One sample has been run with both stearic and lauric acids.
II. EXPERIMENTAL

A. Sample-Drying Methods

Several different methods of drying powders before determination of their surface areas have been compared to determine the minimum drying time and most convenient method that could be utilized in the radiostearic acid technique. Samples were dried in an oven at 110°C and atmospheric pressure, in a vacuum oven at 120°C and approximately 100 mm of pressure, in the BET adsorption apparatus at 120°C and 0.1 mm of pressure, and at 100°C and approximately 100 mm of pressure in a flask having a stopcock in the neck for introduction of the sorbate solution to the sample without admission of air. These different drying techniques and several different drying times were tested in surface area determinations on zinc sulfide, abrasive alumina, titania, silica, clay, sodium carbonate, and sodium bicarbonate powders. The concentration of the stearic acid solutions used was 4.0 grams per liter and the specific activity was 0.25 millicurie per gram of stearic acid. A temperature of 14°C was used in all but three of the determinations. The latter were run at 21°C because the refrigerated water bath was not operable at the time. Data from these experiments are given in Table I.

B. Sorbate-Sorbent Contact Time

Several surface area determinations were designed to determine whether or not equilibrium between sorbent and sorbate is approximated sufficiently after one hour to give the same surface area values as are obtained when the system is allowed to equilibrate for several hours. One of two powder samples dried under identical conditions was allowed to equilibrate with the stearic acid solution overnight while the other was in the solution only one hour. These data are also included in Table I.

C. Sorption of Shorter Fatty Acid Molecules

The specific surface area of duplicate samples of powdered charcoal was determined by radiostearic acid (C18) sorption and radiolauric acid (C12) sorption. In both cases, acid concentrations of 0.014 mole per liter of benzene solution and 0.246 millicurie per gram of acid were used. The results from this experiment are presented in Table II.
TABLE I
COMPARISON OF DRYING METHODS, DRYING TIMES, AND SORBENT-SORBATE CONTACT TIMES IN SPECIFIC SURFACE AREA ($S_W$) DETERMINATIONS BY RADIOSTEARIC ACID SORPTION

<table>
<thead>
<tr>
<th>Powder Sample</th>
<th>$S_W$ by BET Method $^1$ (M$^2$/Gm)</th>
<th>Drying Method$^2$</th>
<th>Drying Time (Hours)</th>
<th>Sorbent-Sorbate Contact Time (Hours)</th>
<th>$C/C_0$ $^3$</th>
<th>$S_W$ by Radio- Stearic Acid (M$^2$/Gm)</th>
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</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>3.7</td>
<td>A</td>
<td>15</td>
<td>15</td>
<td>0.29</td>
<td>3.96</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.7</td>
<td>B</td>
<td>4</td>
<td>15</td>
<td>0.28</td>
<td>4.0</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.7</td>
<td>D</td>
<td>5-1/2</td>
<td>15</td>
<td>0.33</td>
<td>3.5</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.7</td>
<td>A</td>
<td>2</td>
<td>1</td>
<td>0.32</td>
<td>3.5</td>
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<tr>
<td>ZnS</td>
<td>3.7</td>
<td>A</td>
<td>2</td>
<td>15</td>
<td>0.35</td>
<td>3.36</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.7</td>
<td>A</td>
<td>15</td>
<td>1</td>
<td>0.36</td>
<td>3.57</td>
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<tr>
<td>Abrasive (Al$_2$O$_3$)</td>
<td>2.29</td>
<td>A</td>
<td>1</td>
<td>1</td>
<td>0.51</td>
<td>1.10</td>
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<td>Abrasive (Al$_2$O$_3$)</td>
<td>2.29</td>
<td>A</td>
<td>8</td>
<td>1</td>
<td>0.48</td>
<td>1.41</td>
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<td>Abrasive (Al$_2$O$_3$)</td>
<td>2.29</td>
<td>B</td>
<td>4</td>
<td>1</td>
<td>0.48</td>
<td>1.39</td>
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<tr>
<td>Abrasive (Al$_2$O$_3$)</td>
<td>2.29</td>
<td>D</td>
<td>7</td>
<td>1</td>
<td>0.43</td>
<td>2.19</td>
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<td>Abrasive (Al$_2$O$_3$)</td>
<td>2.29</td>
<td>A</td>
<td>15</td>
<td>1</td>
<td>0.51</td>
<td>1.4</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>3.36</td>
<td>A</td>
<td>3</td>
<td>1.25</td>
<td>0.64</td>
<td>1.19</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>3.36</td>
<td>B</td>
<td>3</td>
<td>1.25</td>
<td>0.58</td>
<td>1.92</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>3.36</td>
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<td>3</td>
<td>1.25</td>
<td>0.59</td>
<td>1.72</td>
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<td>TiO$_2$</td>
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<td>B</td>
<td>5</td>
<td>4</td>
<td>0.49</td>
<td>1.44</td>
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<tr>
<td>TiO$_2$</td>
<td>2.2</td>
<td>A</td>
<td>1</td>
<td>1</td>
<td>0.51</td>
<td>0.94</td>
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<tr>
<td>TiO$_2$</td>
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<td>B</td>
<td>4</td>
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<td>0.52</td>
<td>0.87</td>
</tr>
<tr>
<td>TiO$_2$</td>
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<td>A</td>
<td>84</td>
<td>1</td>
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<td>0.76</td>
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<tr>
<td>TiO$_2$</td>
<td>2.2</td>
<td>A</td>
<td>2</td>
<td>15</td>
<td>0.53</td>
<td>0.95</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>2.2</td>
<td>D</td>
<td>4</td>
<td>1</td>
<td>0.56</td>
<td>0.78</td>
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<tr>
<td>Na$_2$CO$_3$</td>
<td>0.6</td>
<td>A</td>
<td>6</td>
<td>1</td>
<td>0.23</td>
<td>3.74</td>
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<tr>
<td>Na$_2$CO$_3$</td>
<td>0.6</td>
<td>A</td>
<td>15</td>
<td>1</td>
<td>0.10</td>
<td>4.36</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>0.6</td>
<td>D</td>
<td>4</td>
<td>1</td>
<td>0.57</td>
<td>0.90</td>
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<tr>
<td>NaHCO$_3$</td>
<td>2.09</td>
<td>D</td>
<td>6</td>
<td>1</td>
<td>0.56</td>
<td>3.25</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>2.09</td>
<td>A</td>
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<td>1</td>
<td>0.006</td>
<td>5.73</td>
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<tr>
<td>NaHCO$_3$</td>
<td>2.09</td>
<td>A</td>
<td>15</td>
<td>1</td>
<td>0.007</td>
<td>5.48</td>
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<tr>
<td>SiO$_2$</td>
<td>26.6</td>
<td>A</td>
<td>15</td>
<td>1</td>
<td>0.64</td>
<td>4.37</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>26.6</td>
<td>D</td>
<td>20</td>
<td>1</td>
<td>0.67</td>
<td>1.48</td>
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<tr>
<td>Clay</td>
<td>14.0</td>
<td>A</td>
<td>15</td>
<td>1</td>
<td>0.61</td>
<td>4.12</td>
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</tbody>
</table>

$^1$ Nitrogen Adsorption by the Brunauer-Emmet-Teller Method.

$^2$ A - in oven at 110° C, atmospheric pressure; B - in vacuum oven at 120° C, approximately 100 mm of pressure; C - in BET apparatus at 120° C, 0.1 mm of pressure; D - in flask with stopcock to prevent admission of air, at 100° C and approximately 100 mm pressure.

$^3$ Equilibrium concentration/saturation concentration at appropriate temperature.
TABLE II

SPECIFIC SURFACE AREA ($S_w$) DETERMINATIONS BY SORPTION
OF STEARIC AND LAURIC ACIDS ON CHARCOAL*

<table>
<thead>
<tr>
<th>Number</th>
<th>Acid</th>
<th>Initial Counts (Counts/Min)</th>
<th>Final Counts (Counts/Min)</th>
<th>Initial Concentration (Gm/L)</th>
<th>$S_w$ (M^2/Gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stearic</td>
<td>8793</td>
<td>8091</td>
<td>4.03</td>
<td>61.7</td>
</tr>
<tr>
<td>2</td>
<td>Lauric</td>
<td>5161</td>
<td>4597</td>
<td>2.86</td>
<td>63.6</td>
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</tbody>
</table>

*$S_w$ by BET = 400 m^2/gm. Charcoal samples weighed 0.1 gram.

The lauric acid-1-carbon-14 for this work was purchased, in the acid form, from the California Corporation for Biochemical Research. The sodium salt of caproic acid-1-carbon-14 was obtained from the same company. The inert, or carrier, forms of both acids are Matheson Coleman and Bell's research grade, approximately 98 per cent pure.
III. DISCUSSION AND CONCLUSIONS

For many materials, particularly basic compounds such as sodium carbonate and sodium bicarbonate or highly hygroscopic materials such as silica, the exclusion of air from the sample before and during the addition of sorbate solution is mandatory. The basic materials will react quickly with stearic acid in the presence of very small amounts of water and thus give surface area values that are too high, while for silica and similar materials the presence of any sorbed moisture on the surface reduces the amount of fatty acid that can be sorbed and thus yields deceptively low surface area values. Consequently, when the properties of a powder are either unknown or else known to be basic or hygroscopic, the powder should be dried and evacuated in a sample flask with a stopcock for admitting fatty acid solution in the absence of air.

Apparently the sorption equilibrium between sorbent powders and stearic acid solutions is approached sufficiently in one hour to give good surface area values.

Required drying times vary. For an inert sample such as zinc sulfide, drying for only 2 hours in an oven at 110°C and atmospheric pressure is sufficient. Moisture-retaining materials such as alumina and silica require 7 or 8 hours of drying at low (100 mm or less) pressure.

From the comparison of stearic acid and lauric acid sorbed by charcoal, shown in Table II, it appears that the pores in this powder are not large enough to admit more 12-carbon chains than 18-carbon chains. Therefore no conclusions can be drawn about the feasibility of average-pore-size measurements utilizing fatty acids of several different chain lengths.
IV. FUTURE PROGRAM

In the immediate future, several specific surface area determinations will be run with caproic, lauric, and stearic acids in order to judge the feasibility of the proposed porosity measurements.

Respectfully submitted:

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Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief
Chemical Sciences Division
AN INVESTIGATION OF THE USE OF RADIOACTIVE ISOTOPES FOR DETERMINING THE SURFACE AREA OF POWDERED MATERIALS BY SORPTION METHODS

By

MARGARET C. KORDECKI and MIRIAM B. GANDY

COVERING THE PERIOD
1 JULY 1960 to 30 SEPTEMBER 1960
Printed 10 October 1960

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TASK NO. III, CONTRACT AUTHORIZATION NO. 1A-59-34
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SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia
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ABSTRACT

Experimental work has been conducted to determine the best solvents, plating techniques, and other details for surface area determinations with lauric acid-1-\( ^1\)C\( ^{14}\) (\( \text{C}_{12}\text{H}_{26}\text{O}_{2} \)) and hexanoic acid-1-\( ^1\)C\( ^{14}\) (\( \text{C}_{6}\text{H}_{14}\text{O}_{2} \)). The sodium salt of the latter was used in methanol solution, while both benzene and methanol solutions of lauric acid were used for determinations with high-surface carbon black and silica. Stearic acid sorption by the same samples was also determined in order to check the effect of carbon-chain length on the apparent surface area values obtained by fatty acid sorption.

Also, a statistical treatment of the data obtained in determinations utilizing acids of different chain lengths has been postulated to estimate pore size distributions in high-surface powders. Cumulative plots were made of the number of carbons in the fatty acid chain versus the percentage of pores under the size required to accommodate chains of the specified length. (The latter figure was calculated by dividing the difference between the BET value and the fatty acid surface area by the BET value and multiplying by 100 per cent.) A calculation was also made of the approximate size of an idealized pore that would accommodate a perfectly fitted monomolecular layer of a fatty acid of known length.
TABLE OF CONTENTS

Page

TITLE PAGE ......................................................... 1
ABSTRACT ........................................................... ii
TABLE OF CONTENTS .................................................. iii
LIST OF FIGURES ................................................... iv
LIST OF TABLES .................................................... iv
I. INTRODUCTION ................................................... 1
II. EXPERIMENTAL .................................................. 1
   A. Plating and Self-Absorption .............................. 1
   B. Surface Area Determinations .............................. 2
III. DISCUSSION AND CONCLUSIONS .............................. 5
   A. Discrepancies Between Specific Surface Areas Obtained by Fatty
      Acid Sorption and by Nitrogen Adsorption .............. 5
   B. Tentative Treatment of Fatty Acid Sorption Data for Estimating
      Pore Size Distribution ................................. 6
IV. SUMMARY ........................................................ 11
V. PUBLICATIONS .................................................... 11
VI. FUTURE WORK ................................................... 12

This report contains 12 pages.
LIST OF FIGURES

1. Pore Size Distributions ........................................... 8
2. An Idealized Pore .................................................. 9

LIST OF TABLES

I. DATA FROM PLATING TESTS AND SELF-ABSORPTION STUDY WITH METHANOL SOLUTIONS OF SODIUM HEXANATE ........................................... 3
II. SPECIFIC SURFACE AREAS OF CHARCOAL AND SILICA SAMPLES .......... 4
I. INTRODUCTION

During the past quarter, laboratory work continued on determining appropriate solvents, plating techniques, and other details preparatory to utilizing several different carbon-14-labelled fatty acids to determine the pore size of powders. Saturated fatty acids with chains of 6, 12, and 18 carbon atoms have been used in surface area determinations of high-surface powders. In addition, study of the literature has yielded data useful for postulating a tentative treatment of fatty acid sorption data for comparison of pore size distribution in powders.

II. EXPERIMENTAL

A. Plating and Self-Absorption

As each new acid was added to the experimental determinations, new problems in precision plating of replicate samples were encountered. Differences in solubility and surface tension are largely responsible for the difficulties. Consequently, considerable time was expended in tests to establish the best plating procedures, the best solvent, and the extent of self-absorption for hexanoic and lauric acids. Since the former is infinitely soluble in benzene and methanol, its sodium salt was used in methanol solutions. Initial plating tests utilized only the inert acids, and were judged visually. Teflon discs, aluminum planchets, watch glasses, and watch glasses prewetted with dilute insulin were tested. Of these, only the aluminum pans were entirely unsatisfactory. However, methanol solutions of sodium hexanate have such a low surface tension that aliquots as large as 0.05 ml "crawl" out of the 25-mm watch glasses that have been used for 0.1-ml stearic acid aliquots. It was found that 40-mm watch glasses will accommodate 0.05 ml of the hexanate solu-
tions, and good uniform deposits are obtained if the glass has been thoroughly cleaned (e.g., with Alconox detergent). Tests utilizing the radioactive acids, however, showed that concentrated solutions formed more cohesive deposits that, due to self-absorption and to their surprisingly smaller deposit diameter, gave counts considerably smaller than those obtained from dilute solutions. Results of the plating tests and self-absorption study with sodium hexanate are given in Table I.

B. Surface Area Determinations

Stearic and lauric acids and sodium hexanate were utilized in surface area determinations on porous powders—charcoal and several different silica samples. In some cases both stearic and lauric acid were dissolved in benzene for determinations of the specific surface area of charcoal, but in later tests all of the sorbates used with charcoal samples were dissolved in methanol, which, according to Galbraith, et al.,\(^1\) competes less for the surface of carbons than does benzene. Data from all of the surface area determinations made during this quarter are given in Table II.

---

<table>
<thead>
<tr>
<th>Description of Plate</th>
<th>Concentration of Solution (Gm/Liter)</th>
<th>Aliquot Size (ML)</th>
<th>No. of Plates</th>
<th>Average Counts (Counts/Min)</th>
<th>Avg. Dev. in Replicate Plates (%)</th>
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</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>63.8</td>
<td>0.05</td>
<td>4</td>
<td>1248</td>
<td>3.8</td>
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<td>Aluminum</td>
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<td>0.05</td>
<td>4</td>
<td>1982</td>
<td>0.5</td>
</tr>
<tr>
<td>Aluminum</td>
<td>31.9</td>
<td>0.05</td>
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<td>820</td>
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<td>4</td>
<td>415</td>
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<td>1716</td>
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<td>0.10</td>
<td>2</td>
<td>1171</td>
<td>4.1</td>
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<td>31.9</td>
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<td>1354</td>
<td>10.3</td>
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<td>2</td>
<td>139</td>
<td>11.5</td>
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<td>40-mm watch glass; insulin&lt;sup&gt;a&lt;/sup&gt;</td>
<td>42.5</td>
<td>0.05</td>
<td>2</td>
<td>673</td>
<td>0.6</td>
</tr>
<tr>
<td>40-mm watch glass; one with insulin, 2 without</td>
<td>30.1</td>
<td>0.05</td>
<td>3</td>
<td>505</td>
<td>1.4</td>
</tr>
<tr>
<td>40-mm watch glass</td>
<td>11.4</td>
<td>0.05</td>
<td>2</td>
<td>219</td>
<td>6.2</td>
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<td>40-mm watch glass; insulin</td>
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<td>0.05</td>
<td>2</td>
<td>148</td>
<td>8.9</td>
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<td>5.6</td>
<td>0.05</td>
<td>2</td>
<td>123</td>
<td>10.6</td>
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<td>0.05</td>
<td>3</td>
<td>152</td>
<td>7.4</td>
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<td>5.3</td>
<td>0.10</td>
<td>1</td>
<td>250</td>
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<td>25-mm watch glass</td>
<td>5.3</td>
<td>0.01</td>
<td>4</td>
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<td>21.1</td>
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<td>40-mm watch glass; 2 with insulin, 2 without</td>
<td>3.2</td>
<td>0.05</td>
<td>4</td>
<td>92</td>
<td>4.9</td>
</tr>
</tbody>
</table>

<sup>a</sup>In these tests, between 0.05 and 0.10 ml of insulin (diluted 1:100) was added to and then removed from watch glasses by means of a hypodermic needle and syringe.
TABLE II
SPECIFIC SURFACE AREAS OF CHARCOAL AND SILICA SAMPLES

<table>
<thead>
<tr>
<th>Powder</th>
<th>Sorbate</th>
<th>Solvent</th>
<th>Initial Sorbate Concentration (Gm/Liter)</th>
<th>Temp. of Determination (°C)</th>
<th>C/C₀</th>
<th>Specific Surface Area BET (Meter²/Gm)</th>
<th>Fatty Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td>Lauric acid</td>
<td>Benzene</td>
<td>2.93</td>
<td>14</td>
<td>0.003</td>
<td>400</td>
<td>64.7</td>
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<td>Stearic acid</td>
<td>Benzene</td>
<td>4.02</td>
<td>14</td>
<td>0.62</td>
<td>400</td>
<td>63.6</td>
</tr>
<tr>
<td>Silica</td>
<td>Lauric acid</td>
<td>Benzene</td>
<td>200.9</td>
<td>15</td>
<td>0.34</td>
<td>208</td>
<td>244</td>
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III. DISCUSSION AND CONCLUSIONS

A. Discrepancies Between Specific Surface Areas Obtained by Fatty Acid Sorption and by Nitrogen Adsorption

There are several factors to be considered when a powder's specific surface area obtained by fatty acid sorption is lower than the value obtained by the BET nitrogen adsorption method. First, there may be in the particles pores that are large enough to admit sufficient nitrogen to cover this internal surface but are too small to accommodate the number of larger, fatty acid molecules that would be required to cover the internal surface. Indeed, a large pore with a small opening to it could screen out all fatty acid molecules. On the other hand, if fine capillaries exist in the particles, gaseous nitrogen may actually condense, by the phenomenon known as capillary condensation, thereby yielding deceptively high surface area values. Second, the solvent may have a strong affinity for some particular powders and in such a case it would compete with the fatty acid for available sites on the surface. Third, in some cases the fatty acid may lie parallel to the surface instead of exhibiting the perpendicular orientation occasioned by a strong attraction between the polar end of the acid molecule and surfaces having bonds either ionic or strongly polar in nature. Such a parallel orientation has been claimed by Gasser and Kipling\(^2\) for fatty alcohols on charcoal.

The effect of solvent competition for powder surface can be avoided by careful selection of solvents. The effect of parallel orientation of the fatty acid at powder surfaces is not a problem with most materials, e.g., metal powders, metal oxides, salts, and clays. Thus, by eliminating the solvent

competition and by using systems in which the orientation of the fatty acid is definitely known, as well as its correct-sectional area in this particular orientation, the prime factor in cases of surface areas that are lower by fatty acid sorption than by nitrogen adsorption becomes porosity (and/or capillarity). Consequently, with sufficient data and by appropriate mathematical treatment of such data, a reasonable estimation of the pore size distribution of such a sample should be possible.

B. Tentative Treatment of Fatty Acid Sorption Data for Estimating Pore Size Distribution

If the pores of a powder are considered to have a random size distribution, a statistical method similar to that used in studying particle size distribution should be appropriate for the estimation of pore size distribution from data on the sorption of several different fatty acids by a powder. If one overlooks the possibility of capillary condensation in nitrogen adsorption and assumes surface areas obtained by such a method as the well known BET to give the correct maximum specific surface area, then the difference between the surface indicated by this method and by sorption of fatty acids can be assumed to be due to the inaccessibility of some of the pores to the acid.

Lemieux and Morrison\(^3\) have studied the sorption of the shorter fatty acids--acetic, propionic, butyric, and valeric--by different charcoals, Bruns\(^4\) has studied the sorption on activated charcoal of fatty acids with from one

---


through six carbons in the chain, and Linner and Williams\(^5\) used acetic, propionic, butyric, and valeric acids on charcoal. When data from these studies were used in cumulative plots of per cent undersize versus either the number of carbons in the acid chain or the actual length of the acid chain (some chain lengths in the literature were measured; others were calculated) on log-probability paper and on arithmetic probability paper, in many cases a straight line was obtained. Since a straight line from such plots is a fair indication of a random distribution in particle size studies,\(^6\) it follows that the pore sizes of these charcoals probably had a random distribution, at least over the range studied. Unfortunately, neither data obtained in this laboratory nor from the literature extends over a large range of acid length.

Figure 1 is a log-probability plot of data (from Lemieux and Morrison\(^7\)) of fatty acid sorption from aqueous solutions by three charcoals and of data obtained in this laboratory for fatty acid sorption from methanol by charcoal. The percentages were obtained by dividing the difference between the fatty acid surface area and the BET surface area by the BET value. Extensions of the lines presented in this figure could possibly curve either up or down, as shown by the dotted lines. However, even if the probability plot is not a straight line, easily defined by its mean (at the 50-per-cent point) and by its standard deviation (the point at 84 per cent divided by the 50-per-cent reading, or the latter divided by the 16-per-cent point), the plots still lend themselves to interpretation of size distribution data. For example, if curve A of Figure

---


Figure 1. Pore Size Distributions.
l actually should curve as indicated by the dotted lines, essentially all of
the pores of this sample must fall between two sizes—the size large enough
for its internal surface to be covered by acids with 20-carbon chains and the
size that will accommodate only a monolayer of 2-carbon acid chains.

The problem then becomes the estimation of the dimensions of pores that
can accommodate a monolayer of acid molecules of a known chain length. In
order to obtain numerical values for pore size, certain assumptions must be
made. By assuming the pores to be spherical, with an opening larger than the
cross-sectional area of a fatty acid at its larger end (approximately 25
square angstroms), the geometry of spheres can be utilized in the interpreta-
tion. Although unrealistic, this assumption can be used to obtain numbers
useful for comparisons between different samples of the same material.

Consider Figure 2 below, in which a spherical pore is pictured with the
polar end of the fatty acid molecules in a monolayer attached to its internal

Figure 2. An Idealized Pore.
surface. If the cross-sectional areas of all fatty acid chains are, as stated by Markley,\(^8\) 25 Å\(^2\) at the polar -COOH end of the molecule and 20 Å\(^2\) throughout the rest of the chain of CCH\(_2\) groups, the size of a spherical pore that could accommodate a monolayer of an acid of known length packed perfectly, in perpendicular orientation to the internal surface, can be calculated.

If \(n\) is the number of molecules in the monolayer, then the internal surface area of the pore equals \(n \times 25 \text{ Å}^2\), and the internal surface of the monolayer facing the spherical void is \(n \times 20 \text{ Å}^2\). Let the internal surface area of the pore be \(S_t\). Then

\[
S_t = \pi (D_t)^2 = \pi (D_1 + 2L)^2 = n \times 25 \text{ Å}^2,
\]

and

\[
S_1 = \pi (D_1)^2 = n \times 20 \text{ Å}^2,
\]

where \(D_t = \text{total diameter of the pore}, = (D_1 + 2L)\),

\(D_1 = \text{diameter of the spherical void}\),

\(S_1 = \text{area of the void or inner area of the monolayer}\),

and \(L = \text{the length of the fatty acid chain in angstroms}\).

By substitution,

\[
\pi (D_1 + 2L)^2 = \frac{\pi (D_1)^2 \times 25 \text{ Å}^2}{20 \text{ Å}^2},
\]

which can be solved for \(D_1\).

If the previously-mentioned work indicating that fatty alcohols lie parallel to charcoal surfaces should hold true for fatty acid monolayers on charcoal, then the described method of estimating pore dimensions would not

apply to charcoals. Therefore no such calculations have been made for the charcoal data plotted in Figure 1. Another approach would be necessary for monolayers of parallel-oriented molecules. Because of the uncertainty in the case of attachment to charcoal, it seems that experiments to determine pore size distribution should be confined to other materials, e.g. clays and silicas, having enough polar character to attract the polar end of the fatty acids.

IV. SUMMARY

Experimental work has been conducted to determine the best solvents, plating techniques, and other details for surface area determinations with lauric (C\(_{12}\)H\(_{26}\)O\(_2\)) and hexanoic (C\(_{6}\)H\(_{14}\)O\(_2\)) acids. Since the latter is very soluble in benzene, alcohol, and water, its sodium salt was used in methanol solution for surface area determinations. Lauric acid was used in both benzene and methanol solutions. Determinations on high-surface carbon black and silica were run with stearic acid, lauric acid, and sodium hexanate. More acids, especially acetic, and perhaps others, are to be added to the list of those now in use. It appears that, by statistical treatment of data obtained in surface area determinations with several different fatty acids, estimation of pore size distribution should be possible. However, not enough experimental data have been collected yet to give this mathematical treatment a good trial. Work on charcoal has shown more sorption of short chains than long chains, but this could be due, in part, to the effect of fatty acid orientation.

V. PUBLICATIONS

During the last quarter a technical note entitled "Precision Plating of Stearic Acid-1-Carbon-\(^{14}\) from Benzene Solutions" has been accepted for publication in the International Journal of Applied Radiation and Isotopes.
VI. FUTURE PROGRAM

In the immediate future four different saturated fatty acids—acetic, hexanoic, lauric, and stearic—labelled with carbon-14 will be used to determine the specific surface area of high-surface silica and clay samples. The data will be subjected to the statistical treatment described for estimating the pore size distribution. If the results are promising, other acids, possibly formic, which has only one carbon, and a long one with 20 or 22 carbons in the chain, may be added to those used for surface area determinations.

Respectfully submitted,

U
Margaret C. Kordecki
Project Director

Approved:

Fred Siciliano
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division
AN INVESTIGATION OF THE USE OF RADIOACTIVE ISOTOPES FOR DETERMINING THE SURFACE AREA OF POWDERED MATERIALS BY SORPTION METHODS

By

MARGARET C. KORDECKI and MIRIAM B. GANDY

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AIKEN, SOUTH CAROLINA

Performed for
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OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND
ABSTRACT

The sorption of straight-chain fatty acids of several different lengths by a few powders, particularly a high-surface carbon black and a high-surface silica, has been studied. Difficulties were incurred in efforts to prepare, by neutralization of the shorter, liquid fatty acids, uniform precipitates for radioassay by end-window counter, and substitution of sodium salts for liquid acids in the determinations also led to plating difficulties. Therefore sorption of the shorter acids was assayed by titration with standard base. Lauric and stearic acids were measured by radioassay.

Methanolic and aqueous solutions were used in carbon black studies, and benzene solutions were used with silica samples. Because of their great solubility in the solvents, the liquid acids must be tested at four or more different concentrations for construction of sorption isotherms. The point of maximum sorption is then selected for comparison of the powder's ability to sorb different acids. Isotherms completed for the sorption of acetic acid and hexanoic acid by high-surface silica show almost twice as much sorption of the shorter acid. The specific surface area obtained from acetic acid data was 179.5 square meters per gram, which is close to the nitrogen adsorption (BET) value of 193.
**TABLE OF CONTENTS**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
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<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
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<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
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<td>TABLE OF CONTENTS</td>
<td>iii</td>
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<tr>
<td>LIST OF TABLES</td>
<td>iv</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. EXPERIMENTAL</td>
<td>2</td>
</tr>
<tr>
<td>III. DISCUSSION AND CONCLUSIONS</td>
<td>6</td>
</tr>
<tr>
<td>A. Choice of Solvents</td>
<td>6</td>
</tr>
<tr>
<td>B. The Liquid Acids</td>
<td>7</td>
</tr>
<tr>
<td>C. Particle Size Distribution of High-Surface Silica</td>
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</tr>
<tr>
<td>IV. FUTURE PROGRAM</td>
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This Report Contains 9 Pages.
LIST OF TABLES

I. SORPTION OF FATTY ACIDS BY CARBON BLACK (BET = 400 m²/gm) .................. 3

II. SORPTION OF FATTY ACIDS FROM METHANOL ........................................ 4

III. SORPTION OF FATTY ACIDS FROM BENZENE BY HIGH-SURFACE SILICA (BET = 193 m²/gm), MEASURED BY ACID-BASE TITRATION ..................... 5
I. INTRODUCTION

This report summarizes the work performed from October 1, 1960, to December 31, 1960. The purpose of the work under this contract is to investigate the use of radioactive tracer atoms in fatty acids as a means of making accurate surface area measurements on low-surface powders and of determining pore size distributions in high-surface materials.

During this report period work has been concentrated on comparing the sorption of several different fatty acids by one powder in order to estimate its pore size distribution. It has been postulated that the sorption of fatty acids by a highly porous powder will increase with decreasing length of the fatty acid chain, and give a surface area value equal to the nitrogen adsorption value when the acid used is small enough to enter all the pores and form a monomolecular layer on their inner surfaces. The sorption of several different acids—stearic, lauric, hexanoic, acetic, and formic—by various powders, particularly a high-surface carbon black and a high-surface silica, was studied. Because of bonding that occurs between some solvents and powders, comparisons were made between methanolic, benzene, and, in the case of carbon, aqueous solutions of the acid sorbates.
II. EXPERIMENTAL

Because of the attraction of benzene to carbon blacks and graphites, methanol and water solutions have been utilized with the carbon black (BET value = 400 square meters per gram) that has been used for studies aimed at pore size determination during this and the preceding quarter. Fatty acid sorption data obtained for this carbon sample during the report period are presented in Table I.

Surface area determinations utilizing methanol solutions of several different fatty acids and their salts--hexanoic acid, acetic acid, formic acid, sodium hexanate, and sodium acetate--were made on several different powders. Results in most cases were so much lower than the BET surface areas, that adsorption of methanol by the powders was suspected. Consequently, methanolic solutions of stearic acid were used to check samples on which benzene solutions of stearic acid had earlier given results that agreed with the BET surface areas. Tests indicated that methanol is not a favorable solvent for sorption studies with some powders, notably calcium sulfate and silica. Data for several different powders are given in Table II.

A high-surface silica (BET surface area = 193 square meters per gram) is being used for sorption studies utilizing several different acids in benzene solutions. Radioassay is being utilized where possible (with stearic and lauric acids), and titration with standard potassium hydroxide is being used for the shorter acids (formic through hexanoic). A sorption isotherm is being constructed for each acid, in order to determine the concentration required for maximum sorption. The maximum value for each acid will then be utilized in plots such as that of cumulative per cent versus carbons in the acid chain (see Quarterly Technical Status Report No. 5), and perhaps other treatments for estimating the pore size distribution of this silica. Data obtained to date are given in Table III.
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TABLE I

SORPTION OF FATTY ACIDS BY CARBON BLACK ($BET = 400 M^2/Gm$)
### TABLE II

**SORPTION OF FATTY ACIDS FROM METHANOL**

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TABLE III
SORPTION$^a$ OF FATTY ACIDS FROM BENZENE BY HIGH-SURFACE SILICA
(BET = 193 $M^2/Gm$), MEASURED BY ACID-BASE TITRATION

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</tbody>
</table>

$^a$ At room temperature: 75-78°F.
III. DISCUSSION AND CONCLUSIONS

A. Choice of Solvents

Various factors influenced the choice of solvents. Benzene, for example, has been found to adhere to graphite and carbon blacks\(^1\) and thus would cause low surface area values for these materials. Aqueous solutions of the lower aliphatic acids, acetic through hexanoic, have been used in some investigations comparing the effects of different methods of carbon catalyst activation.\(^2\) However, if it is desired to study the sorption of acids ranging from formic up through acid chains of 18 or more carbons, the same solvent should be used for each acid. Since the higher acids have practically no water solubility, methanol probably would be the best solvent for pore size distribution studies on carbon blacks. Methanolic solutions of the solid fatty acids have been found very difficult to plate for radioassay, however. The low surface tension of such solutions causes them to "creep" in such a way that very irregular, unsatisfactory deposits of the solid are obtained. Teflon seems to be the best substrate for methanolic solutions, but even on Teflon the average deviation in replicate plates is often as high as 15 per cent. If a liquid scintillation counter were available to count solution aliquots and avoid the plating problem, methanol could be conveniently used. However, in the absence of such a counter a different solvent is needed for carbon black studies utilizing radioassay as the analytical tool.


Benzene should be appropriate for most other powders. All of the straight-chain fatty acids from formic through acetic are benzene-soluble to some degree. In addition, powders with some polar character have less affinity for benzene than they do for the more polar solvents.

B. The Liquid Acids

The liquid acids cannot be safely assayed with an end-window Geiger counter, since even those of higher molecular weight have enough vapor pressure that aliquots of the liquid left uncovered for counting could contaminate the counter and possibly the laboratory. (Thin films of mylar or other materials over the liquid absorb the weak Beta rays of carbon-14.) Attempts to plate hexanoic acid as its solid sodium or potassium salt by pipetting aliquots on to concentrated solutions of the respective hydroxides were unsuccessful because of the slow reaction rate. Application of heat to such plates increased the vaporization of unreacted acid more than it increased the reaction rate. Consequently, surface area determinations utilizing sodium salts of hexanoic acid-l-carbon-14 and of acetic acid-l-carbon-14 were attempted. These salts are not soluble enough in benzene to permit radioassay by counting a small volume of the benzene solution, and their methanolic solutions have low surface tensions that result in very poor plates. Here, again, a liquid scintillation counter would be ideal, since aliquots of the acid or salt solutions could be added to the liquid scintillator and the tube sealed to avoid vapor losses.

In the absence of the desired counting system, it was necessary to turn to acid-base titration for assay of the sorption of liquid fatty acids.

C. Particle Size Distribution of High-Surface Silica

Sorption isotherms for acetic acid and hexanoic acid sorbed from benzene solutions by high-surface silica show a considerable difference. (See Table III.)
The maximum specific surface area (moles sorbed per gram x effective cross-sectional area per mole) was 179.5 square meters for the two-carbon acid and only 93.4 square meters for the six-carbon acid. Apparently, the value is approaching the nitrogen adsorption value (193 square meters by the BET method) as the carbon chain becomes shorter. It is expected that the sorption isotherm for formic acid (one carbon) will show a maximum equal to, if not greater than, the acetic acid maximum and that much lower maximums will be obtained with lauric (12-carbon chain) and stearic (18-carbon chain) acids. If the data obtained during the next month do follow these predictions, they will lend themselves well to an estimation of the pore size distribution in this silica sample.
IV. FUTURE PROGRAM

In the immediate future, data for several more sorption isotherms showing the sorption of fatty acids from benzene by a high-surface silica will be obtained. Formic acid sorption will be determined by titration with standard base, and radioassay will be utilized for lauric acid and stearic acid. If the results are as expected, the sorption of several other acids—probably propionic, butyric, and valeric—by the same silica will be studied. Particle size statistics will be utilized in estimating pore size distribution from the resulting data and previously obtained values.

Respectfully submitted:

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ANNUAL TECHNICAL STATUS REPORT NO. 1
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AN INVESTIGATION OF THE USE OF RADIOACTIVE ISOTOPES FOR
DETERMINING THE SURFACE AREA OF POWDERED MATERIALS BY
SORPTION METHODS

By

MARGARET C. KORDECKI AND MIRIAM L. BARNES

COVERING THE PERIOD
1 APRIL 1959 to 31 MARCH 1960
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AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

REVIEW
PATENT 4-28-60 BY...
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ABSTRACT

The determination of powder surface area by sorption of fatty acids from solutions is an established technique. However, it is not in general use because methods for quantitative analysis of fatty acids lack the desired speed, convenience, and accuracy. This investigation was undertaken to develop a technique for accurate surface area determinations, particularly for relatively low-surface materials, by radioassay of sorbed fatty acids labelled with carbon-14. Such a technique has been developed and consists of the following steps: (1) weigh approximately one gram of oven-dried powder into a round-bottom flask with stopcock above the ground-glass joint at the neck; (2) heat 6 hours at 110°C with Glas-Col heating mantle while simultaneously degassing by vacuum pump; (3) close stopcock, cool sample, and above the stopcock attach a burette filled with radio-stearic acid-benzene solution (7 to 8 grams/liter; 0.1 to 0.2 millicurie/gram of acid); (4) measure 10 ml of solution into the flask, close stopcock, and shake vigorously; (5) let sample equilibrate in water bath one hour at 15°C, with occasional shaking; (6) decant the solution into a centrifuge tube, stopper, and centrifuge briefly; (7) decant to another tube, stopper, and let solution reach room temperature before plating; (8) pipette 0.1-ml aliquots of this solution and of original solution to chilled, 25-mm watch glasses and place in refrigerator for slow solvent evaporation; and (9) count plates with a thin end-window Geiger counter.

To improve the accuracy of this method, an empirical correction for self-absorption (and other factors tending to distort the relation of observed counts to concentration of the plated solutions) is used. It consists of determining the solution concentration from a plot of concentration versus counts obtained by counting plates of several different known concentrations having the same specific activity as the solution used in the surface area determination. The surface area is then calculated from the equation given below.

\[
S_w = \frac{(\text{initial-final}) \text{ moles/ml} \times 10 \text{ ml} \times 6.023 \times 10^{23} \times 20.5 \times 10^{-20} \text{ m}^2/\text{mole}}{\text{sample weight}}
\]
For powders with surface area at the extremes of the range for which this method is applicable (0.1 to approximately 100 m²/gm), the conditions used in these determinations must be modified by, for example, larger sample weights and lower stearic acid concentrations for low surface areas, and small sample weights with high stearic acid concentrations for the larger surface areas.
Annual Technical Status Report No. 1, Project No. A-446-3

TABLE OF CONTENTS

| TITLE PAGE | .................................................. | 1 |
| ABSTRACT | .................................................. | 11 |
| TABLE OF CONTENTS | .................................................. | iv |
| LIST OF FIGURES | .................................................. | v |
| LIST OF TABLES | .................................................. | v |
| I. INTRODUCTION | .................................................. | 1 |
| II. BACKGROUND | .................................................. | 2 |
| A. Fatty Acid Monolayers | .................................................. | 2 |
| B. Surface Area Determinations by Fatty Acid Sorption | .................................................. | 3 |
| III. EXPERIMENTAL WORK | .................................................. | 6 |
| A. Materials and Apparatus | .................................................. | 6 |
| 1. Dry Box | .................................................. | 6 |
| 2. Counters | .................................................. | 6 |
| 3. Stearic Acid Solutions | .................................................. | 6 |
| B. Preliminary Experiments | .................................................. | 6 |
| C. Techniques for Plating Benzene Solutions of Stearic Acid | .................................................. | 8 |
| D. Corrections Applied to Counting Data | .................................................. | 10 |
| E. General Method for Surface Area Determination by Radiostearic Acid Sorption | .................................................. | 15 |
| IV. DISCUSSION AND CONCLUSIONS | .................................................. | 20 |
| A. Materials and Apparatus | .................................................. | 20 |
| 1. Dry Box | .................................................. | 20 |
| 2. Counters | .................................................. | 20 |
| 3. Stearic Acid Solutions | .................................................. | 20 |
| B. Preliminary Experiments | .................................................. | 21 |
| C. Plating Techniques | .................................................. | 21 |
| D. Corrections Applied to Counting Data | .................................................. | 22 |
| E. General Method for Surface Area Determination by Radiostearic Acid Sorption | .................................................. | 23 |
| V. SUMMARY | .................................................. | 25 |
| VI. FUTURE PROGRAM | .................................................. | 27 |

This Report Contains 27 Pages.
LIST OF FIGURES

1. Isotherm for Sorption of Palmitic Acid by Platinum ........ 4
2. Isotherms for Sorption of Stearic Acid from Benzene Solution ... 4
3. Correction Curves for Stearic Acid-1-Carbon-14 Plated from Benzene Solutions .............................................. 14

LIST OF TABLES

I. SPECIFIC SURFACE AREA (S_w) DETERMINATIONS: CLAYS .......... 9
II. DATA FROM TESTS TO DETERMINE THE BEST PLATING TECHNIQUES ... 11
III. DATA FOR CORRECTION CURVES FOR STEARIC ACID SOLUTIONS ........ 13
IV. DATA AND CORRECTIONS FOR SURFACE AREA OF FERRIC OXIDE ....... 15
V. SPECIFIC SURFACE AREA (S_w) DETERMINATIONS: OXIDES, METALS, SALTS, AND GLASS ........................................ 17
VI. AID FOR ESTIMATING VOLUME OF FATTY ACID SOLUTIONS REQUIRED FOR SURFACE AREA DETERMINATIONS ......................... 19
VII. SOLUBILITY OF STEARIC ACID IN GRAMS PER 100 GRAMS OF SOLVENT . 19
I. INTRODUCTION

This report summarizes the work performed from April 1, 1959, to March 31, 1960. The purpose of the work under this contract is to investigate the use of radioactive tracer atoms in fatty acids or stearates in liquid solution as a means of making accurate surface area measurements of relatively low-surface materials.
II. BACKGROUND

A. Fatty Acid Monolayers

It is a well-established fact that certain fatty acid solutions will form unimolecular layers of these acids on water. When properly compressed, straight chain, saturated fatty acids will occupy the same area on the water surface in spite of variations in length of the carbon chains, thereby indicating a vertical orientation of the molecules. The cross-sectional area of fatty acids in such monolayers has been found to be $20.5 \times 10^{-20}$ square meters. The tendency of these acids to produce oriented unimolecular layers suggested to Harkins and Gans that such a layer, if formed at the interface of a liquid and a solid, would serve as a measure of the solid's surface area. Their experiments with oleic acid and titanium dioxide gave results in fair agreement with microscopic measurements.

To produce a fatty acid monolayer on a solid, the affinity of the carboxyl group for the solid must be greater than that of the solvent for the solid. The type of interaction between the monolayer and the solid it covers varies with the system. Chemisorption, physical adsorption, absorption, ion exchange, or a combination of these may occur in monolayer formation. Consequently, the general term "sorption" is used unless there is experimental evidence of the specific nature of the interaction. Smith and Fusek studied the sorption of palmitic acid on nickel and platinum catalysts and found chemisorption indicated by the complete removal of acid from solution when it was present in concentrations lower than that required for complete saturation of the solid surface. Physical adsorption is an equilibrium situation and varies with the concentration unless a significant excess of the acid is present.

Sorption of fatty acids is best illustrated by isotherms in which either the amount of sorbed acid or the surface area of the sorbent powder is plotted

---


as ordinate with either initial concentration or the ratio of the final concentration to saturation concentration as abscissa. Sorption isotherms for chemisorption are horizontal straight lines above the concentration required to saturate the surface with a monolayer. Those for physical adsorption rise sharply and become horizontal only after a certain ratio of equilibrium concentration to saturation concentration \( \frac{C}{C_o} \) has been reached. Figures 1 and 2 are examples of sorption isotherms.

B. Surface Area Determinations by Fatty Acid Sorption

The primary limitation to more general use of fatty acid sorption for routine surface area determinations has been the poor degree of accuracy in quantitative analysis for fatty acids. When a sample is shaken with the fatty acid solution, both the initial \( (C_i) \) and final \( (C) \) concentrations of the acid must be determined accurately. For low surface materials, particularly, the difference between these two concentrations, which is the measure of the sorbed acid, is very small and great accuracy is required to determine it. Among the analytical methods that have been used are conductometric titrations, gravimetric and colorimetric techniques, and film pressure hydrophil balance (Langmuir trough).

Among the powders for which surface areas have been determined by fatty acid sorption are nickel, copper, silver, and iron, carbon, calcium carbonate, clays, titanium dioxide, silica, silicon carbide, copper oxides and

---


Figure 1. Isotherm for Sorption of Palmitic Acid by Platinum (Smith and Fusek\(^3\)).

Figure 2. Isotherms for Sorption of Stearic Acid from Benzene Solution (from data of Greenhill\(^5\)).
zinc oxide,\textsuperscript{9} aluminum, chromium, cobalt, cadmium oxide, ferric oxide, lead oxide, and nickel oxide,\textsuperscript{10} and alumina.\textsuperscript{11} In addition, fatty acid sorption on flat surfaces of iron, gold, and mica has been studied.\textsuperscript{12} Different fatty acids have been compared and found to give similar results for the specific surface area of Raney nickel\textsuperscript{13} and certain other powders.\textsuperscript{14} The effect of different solvents has also been studied, and benzene has been recommended as the best solvent.\textsuperscript{15} Study of the sorption isotherms available in the literature indicates that in most cases one surface area determination is sufficient if the relative concentration ($C/C_0$) is at least 0.3, since most of the known sorption isotherms have become horizontal at this point.


\textsuperscript{13} H. A. Smith and J. F. Fusek, loc. cit.


\textsuperscript{15} Ibid.
III. EXPERIMENTAL WORK

A. Materials and Apparatus

1. Dry Box

A gloved dry box equipped with an air lock was prepared for the mixing, handling, and storing of solutions and samples. Molecular sieve, indicator drierite, and silica gel were used as desiccants. In addition to preventing the solutions and samples from being contaminated by water vapor, the dry box protected the lab from carbon-14 contamination.

2. Counters

End-window Geiger tubes (200NB) and scalers (Nuclear-Chicago, Models 161A and 181A) located in the Radioisotopes building were used.

3. Stearic Acid Solutions

Stearic acid-l-carbon-14 was obtained in one-millicurie quantities from Volk Radiochemical Co., Chicago, and from Tracerlab, Inc., Waltham, Mass. Stock solutions of the radiotracer were prepared by placing one millicurie in a 100-ml volumetric flask and diluting with dry benzene. Aliquots of tracer solution were then used to "tag" solutions of inert stearic acid. The latter material initially was obtained from Matheson Coleman and Bell, East Rutherford, N. J. In later experiments, however, Eastman White Label stearic acid, deemed to be of higher purity, was used.

Initially, reagent grade benzene for these solutions was fractionally distilled and stored over sodium. In later experiments the benzene was not fractionated and was stored over molecular sieve. Use of sodium was discontinued because it was found that minute quantities of sodium or sodium hydroxide were being transferred to the stearic acid solutions where they precipitated some of the acid as sodium stearate.

B. Preliminary Experiments

Preliminary tests were necessary to determine appropriate amounts of radiostearic acid to be added to inert stearic acid. It was desired that plates of the tagged acid counted with the end-window Geiger tube give counts high enough that the counting time for a sample would not add considerably to the total time required for surface area determinations. (Since a total of 10,000 counts is necessary to reduce the random error in counting to one
per cent, a sample plate giving only 1000 counts per minute should be counted
10 minutes to attain the desired accuracy.)

Initial experiments were conducted with kaolin having a specific surface
area, determined by the BET nitrogen adsorption method, of 8 square meters per
gram. One-, two-, and four-gram samples of kaolin were added to 10 ml of
tagged stearic acid solution (concentrations of 2.8 and 17 grams per liter;
specific activities of 0.07, 0.03, and 0.2 millicurie per gram) in volumetric
flasks in the dry box. The stearic acid had been delivered from a 10-ml
burette with Teflon stopcock. The samples were stoppered and allowed to
equilibrate one hour, with occasional manual shaking, at room temperature.
(A magnetic stirrer was used to stir some of the samples until it was found
that the temperature of the mixture was raised considerably.) The solution
was then decanted to a centrifuge tube, stoppered, and briefly centrifuged.
Small aliquots (0.15, 0.10 and 0.05 ml) of the supernatant liquid and of the
original solution were transferred, by pipette and by hypodermic syringe, to
one-inch-square glass plates, air dried, and counted. In some experiments
the ratio of stearic acid to sample weight was varied to determine whether
or not lower concentrations of the carbon-14-tagged acid could be used than
was indicated by available sorption isotherms for the inert acid on kaolin.

The specific surface area was calculated from the number of stearic
acid molecules sorbed and their cross-sectional area. An equation for the
calculations is given below.

\[
S_w = \left( \frac{C_i - C}{C_i} \right) c_1 \times \frac{v}{w} \times 6.023 \times 10^{23} \frac{\text{molecules}}{\text{mole}} \times 20.5 \times 10^{-20} \frac{\text{m}^2}{\text{molecule}} \tag{1}
\]

where

\( C_i \) = counts for the initial solution,
\( C \) = counts for the final or equilibrium solution,
\( c_1 \) = initial concentration in moles/ per milliliter,
\( v \) = milliliters of sorbate solution used,
\( w \) = weight of powder, in grams.

---

16 P. T. Bankston, "Surface Area Measurement of Small Particles by Liquid-
Phase Adsorption of Stearic Acid," Ph.D. Thesis, Georgia Institute of
Technology (1953).
Data for the kaolin samples described above, as well as for other clay samples, are given in Table I.

C. Techniques for Plating Benzene Solutions of Stearic Acid

During the preliminary experiments, great difficulty was experienced in making reproducible plates of the benzene-stearic acid solutions. When two or more aliquots of a solution were transferred to a glass plate, evaporated to dryness, and counted with an end-window Geiger tube, wide deviations were obtained. The technique for counting mounts of infinite thickness, which has been used for fatty acids,\(^{17}\) was not applicable since it measures differences in specific activity, not different concentrations of the same specific activity. A technique developed by Freedman and Hume\(^{18}\) for precision counting of beta radiation from strontium-90 solutions was inapplicable because the laquer applied on top of their liquid samples could be penetrated by only a small percentage of the low-energy beta rays emitted by carbon-14. (Beta rays from strontium-90 are relatively energetic, with an average energy of 0.61 Mev, while the average value for carbon-14 is 0.145.)

Many methods of plating stearic acid from benzene solution were evaluated. Moving the plating procedure from inside the dry box to the lab bench for easier handling of the tools (pipettes, hypodermic syringes, etc.) did not reduce the average deviation between replicate plates plates to the desired value (less than 2 per cent). Automatic micropipettes ("Micropette" by Alfred Bicknell Assn., Cambridge), a 0.25-ml hypodermic syringe and 0.1-ml Mohr measuring pipettes graduated in 0.001-ml divisions were used to transfer solution aliquots to numerous types of substrates. Discs (usually 1-1/4 inch in diameter) were cut of several materials--such as Teflon, tissue paper, emery cloth, filter paper, and emery paper--and used as substrates for plated samples. Also tried were watch glasses, aluminum pans, and glass slides with 15-mm microscope cells glued on them. Samples were plated on watch glasses


### TABLE I
SPECIFIC SURFACE AREA (S\textsubscript{w}) DETERMINATIONS: CLAYS

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample Powder</th>
<th>S\textsubscript{w} by BET (M\textsuperscript{2}/Gm)</th>
<th>Sample Weight (Gm)</th>
<th>Temp. (°C)</th>
<th>Sol. Vol. (ML)</th>
<th>Initial Conc. (Gm/Liter)</th>
<th>C/C\textsubscript{o} \textsuperscript{a}</th>
<th>Beta Radiation Initial (Counts/Minute)</th>
<th>Final (Counts/Minute)</th>
<th>S\textsubscript{w} (M\textsuperscript{2}/Gm)</th>
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<td>3.927</td>
<td>0.60</td>
<td>5995</td>
<td>5536</td>
<td>3.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a}C/C\textsubscript{o} = final concentration/saturation concentration.

\textsuperscript{b}The powder was heated and evacuated in special sample flask described in Section III E.
containing various liquids, e.g. water, nitrobenzene, acetone, amyl acetate, glycerin, and collodion, and on watch glasses and Teflon discs which had been chilled in the refrigerator. The latter were kept cold on a bed of cracked ice during the plating process and were returned to the refrigerator for slow solvent evaporation. Counting data from these tests are given in Table II. Several materials were rejected by visual observation of plates made with inert stearic acid. Of all these plates, the chilled Teflon and chilled watch glasses gave the most consistent results, and plating by 0.1-ml pipettes on chilled, 25-mm watch glasses, followed by evaporation in the refrigerator, was finally adopted as routine procedure.

D. Corrections Applied to Counting Data

Data from several experiments indicated that, at some concentrations of stearic acid, the counts from plated aliquots could not be used directly as a measure of the relative concentrations. Due to the low average energy of beta radiation from carbon-14, some of the radiation is absorbed by the deposited stearic acid and cannot reach the counting tube. In addition, if in an experiment the final and initial concentrations are considerably different, the diameter of deposits from 0.1-ml aliquots of the two concentrations may vary enough to give misleading counts and inaccurate results as calculated by equation (1) in Section III B.

An empirical method was devised to correct for these geometrical factors so that radioassay of the plated solutions would be a more accurate means of analysis. A stearic acid stock solution of the desired specific activity was made and diluted with benzene to several different concentrations. Several 0.1-ml aliquots of each concentration were plated (on chilled watch glasses, as described in Section III C) and counted. The data were corrected for tube dead time, by the method described by Tomlinson, 19 and were plotted as concentration versus counts/minute. From the resulting curve, which was very nearly a straight line at concentrations lower than 7 grams per liter, the concentrations of unknown solutions could be read so long as their


-10-
<table>
<thead>
<tr>
<th>Vol. Instrument</th>
<th>Plating Technique</th>
<th>Substrate</th>
<th>Solution Concentration (Gm/Liter)</th>
<th>Specific Activity of Stearic Acid (Millicurie/Gm)</th>
<th>Number of Plates</th>
<th>Average Sample Count (C/Min)</th>
<th>Average Deviation in Plates (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tissue paper</td>
<td>0.25-ml hypodermic syringe</td>
<td>2.790</td>
<td>0.072</td>
<td>6</td>
<td>1078±19</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>15-mm microscope cell on glass slide</td>
<td>Micropipette</td>
<td>2.790</td>
<td>0.072</td>
<td>3</td>
<td>1134±20</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>Teflon</td>
<td>Micropipette</td>
<td>2.790</td>
<td>0.072</td>
<td>8</td>
<td>2587±29</td>
<td>6.6</td>
<td>5.1</td>
</tr>
<tr>
<td>17.002</td>
<td>Micropipette</td>
<td>2.790</td>
<td>0.072</td>
<td>6</td>
<td>2450±29</td>
<td>7.1</td>
<td>3.4</td>
</tr>
<tr>
<td>Teflon</td>
<td>Micropipette</td>
<td>17.002</td>
<td>0.029</td>
<td>4</td>
<td>1483±70</td>
<td>7.1</td>
<td>3.9</td>
</tr>
<tr>
<td>Teflon</td>
<td>Hypodermic</td>
<td>17.002</td>
<td>0.029</td>
<td>4</td>
<td>1341±67</td>
<td>7.1</td>
<td>3.4</td>
</tr>
<tr>
<td>Teflon</td>
<td>Micropipette</td>
<td>17.002</td>
<td>0.029</td>
<td>4</td>
<td>1765±77</td>
<td>4.5</td>
<td>11.3</td>
</tr>
<tr>
<td>Teflon</td>
<td>Micropipette</td>
<td>17.002</td>
<td>0.029</td>
<td>4</td>
<td>14720±86</td>
<td>11.3</td>
<td>11.3</td>
</tr>
<tr>
<td>Teflon</td>
<td>Micropipette</td>
<td>17.002</td>
<td>0.029</td>
<td>4</td>
<td>13299±88</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Teflon</td>
<td>Micropipette</td>
<td>17.002</td>
<td>0.029</td>
<td>3</td>
<td>2507±60</td>
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<td>1.1</td>
</tr>
<tr>
<td>Teflon</td>
<td>Micropipette</td>
<td>17.002</td>
<td>0.029</td>
<td>4</td>
<td>2925±171</td>
<td>4.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Wet filter paper</td>
<td>Micropipette</td>
<td>17.002</td>
<td>0.029</td>
<td>5</td>
<td>273.9±165</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>Emery cloth discs</td>
<td>Hypodermic</td>
<td>17.002</td>
<td>0.029</td>
<td>4</td>
<td>4681±31</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Teflon</td>
<td>Hypodermic</td>
<td>8.615</td>
<td>0.219</td>
<td>6</td>
<td>14128±84</td>
<td>8.1</td>
<td>8.1</td>
</tr>
<tr>
<td>0.1 ml collodion</td>
<td>Hypodermic</td>
<td>8.615</td>
<td>0.219</td>
<td>4</td>
<td>9064±25</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td>Teflon</td>
<td>Hypodermic</td>
<td>8.615</td>
<td>0.219</td>
<td>4</td>
<td>14128±69</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Tracing paper</td>
<td>Pipette</td>
<td>8.615</td>
<td>0.219</td>
<td>3</td>
<td>13206±81</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Tracing paper</td>
<td>Lambda pipette</td>
<td>8.615</td>
<td>0.219</td>
<td>3</td>
<td>1338±26</td>
<td>4.1</td>
<td>4.1</td>
</tr>
<tr>
<td>Tracing paper</td>
<td>Lambda pipette</td>
<td>8.615</td>
<td>0.219</td>
<td>3</td>
<td>1374±26</td>
<td>3.9</td>
<td>3.9</td>
</tr>
<tr>
<td>Chilled watch glass</td>
<td>Pipette</td>
<td>8.615</td>
<td>0.219</td>
<td>4</td>
<td>12458±79</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Chilled Teflon</td>
<td>Pipette</td>
<td>8.615</td>
<td>0.219</td>
<td>4</td>
<td>14238±84</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Chilled watch glass</td>
<td>Pipette</td>
<td>8.615</td>
<td>0.219</td>
<td>8</td>
<td>13359±67</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Chilled Teflon</td>
<td>Pipette</td>
<td>8.615</td>
<td>0.219</td>
<td>13</td>
<td>15762±73</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>
### TABLE II (Continued)

DATA FROM TESTS TO DETERMINE THE BEST PLATING TECHNIQUES

<table>
<thead>
<tr>
<th>Vol. (ML)</th>
<th>Instrument</th>
<th>Substrate</th>
<th>Solution Concentration (Gm/Liter)</th>
<th>Specific Activity of Stearic Acid (Millicurie/Gm)</th>
<th>Number of Plates</th>
<th>Average Sample Count (C/Min)</th>
<th>Average Deviation in Plates (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>Pipette</td>
<td>Chilled watch glasses</td>
<td>10.79</td>
<td>0.278</td>
<td>10</td>
<td>17225+90</td>
<td>2.4</td>
</tr>
<tr>
<td>0.1</td>
<td>Pipette</td>
<td>Chilled watch glasses</td>
<td>10.79</td>
<td>0.278</td>
<td>12</td>
<td>16490+91</td>
<td>2.8</td>
</tr>
<tr>
<td>0.1</td>
<td>Pipette</td>
<td>Chilled watch glasses</td>
<td>0.108</td>
<td>0.278</td>
<td>3</td>
<td>1929+31</td>
<td>0.9</td>
</tr>
<tr>
<td>0.1</td>
<td>Pipette</td>
<td>Chilled watch glasses</td>
<td>0.108</td>
<td>0.278</td>
<td>3</td>
<td>2046+32</td>
<td>3.0</td>
</tr>
<tr>
<td>0.1</td>
<td>Pipette</td>
<td>Chilled Teflon</td>
<td>10.79</td>
<td>0.278</td>
<td>3</td>
<td>19984+82</td>
<td>1.5</td>
</tr>
<tr>
<td>0.1</td>
<td>Pipette</td>
<td>Chilled Teflon</td>
<td>10.79</td>
<td>0.278</td>
<td>6</td>
<td>20498+83</td>
<td>1.3</td>
</tr>
<tr>
<td>0.1</td>
<td>Pipette</td>
<td>Chilled watch glasses</td>
<td>10.0</td>
<td>0.278</td>
<td>12</td>
<td>14804+86</td>
<td>1.0</td>
</tr>
</tbody>
</table>

a Additional substrates rejected for plates by visual observation of tests made with inert stearic acid solutions were (1) empty watch glasses; (2) watch glasses containing water, amyl acetate, ethylene glycol, or acetone; (3) glass slides with layers of small glass beads glued to them with epoxy resin; and (4) aluminum pans.

b The micropipette used was an automatic "Micropette" (manufactured by Alfred Bicknell Assn., Cambridge, Mass.) adjusted to deliver 0.1 ml. The pipette used was a 0.1-ml Mohr measuring pipette graduated in 0.001-ml divisions; it was filled and emptied by means of a thumbscrew type of pipette filler (Adams Suction Apparatus). The hypodermic syringe was of 0.25-ml capacity with 0.01-ml graduations.

c All of the papers listed here were 3.2-cm discs; they rested on Teflon plates until the solution had dried. Teflon plates were also discs 3.2 cm in diameter.

d Most of the plates were counted on the top shelf under the end-window Geiger tube. A few were counted on the second shelf.
specific activity was the same as that used for the standard curve and if their concentrations did not exceed 8 or 9 grams per liter. (At higher concentrations the plot curves and rises sharply as the plated aliquots approach "infinite thickness." Once the point of infinite thickness has been reached, all higher concentrations give the same count except for differences due to deposit diameter.) Higher concentrations must be diluted before plating.

Such correction curves were made for specific activities of 0.064, 0.127, and 0.246 millicurie per gram. They are shown in Figure 3, with data in Table III. Before applying these correction curves, sample counts were corrected for tube dead time. If found necessary from the count of a standard carbon-14-source that was made at each counting session, they were also corrected for tube response.

### TABLE III

DATA FOR CORRECTION CURVES FOR STEARIC ACID SOLUTIONS

<table>
<thead>
<tr>
<th>Concentration (Gm/Liter)</th>
<th>Specific Activity: 0.064 Millicurie/Gm (Counts/Min)</th>
<th>Specific Activity: 0.127 Millicurie/Gm (Counts/Min)</th>
<th>Specific Activity: 0.246 Millicurie/Gm (Counts/Min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.094</td>
<td></td>
<td>1905</td>
<td></td>
</tr>
<tr>
<td>1.304</td>
<td></td>
<td>3210</td>
<td></td>
</tr>
<tr>
<td>1.919</td>
<td></td>
<td>5000</td>
<td></td>
</tr>
<tr>
<td>2.608</td>
<td></td>
<td>6320</td>
<td></td>
</tr>
<tr>
<td>3.023</td>
<td></td>
<td>3293</td>
<td></td>
</tr>
<tr>
<td>3.260</td>
<td></td>
<td>7520</td>
<td></td>
</tr>
<tr>
<td>3.941</td>
<td></td>
<td>10030</td>
<td></td>
</tr>
<tr>
<td>4.584</td>
<td></td>
<td>12200</td>
<td></td>
</tr>
<tr>
<td>4.62</td>
<td></td>
<td>5309</td>
<td></td>
</tr>
<tr>
<td>5.216</td>
<td></td>
<td>12460</td>
<td></td>
</tr>
<tr>
<td>6.283</td>
<td></td>
<td>15059</td>
<td></td>
</tr>
<tr>
<td>6.520</td>
<td></td>
<td>17194</td>
<td></td>
</tr>
<tr>
<td>7.392</td>
<td></td>
<td>16616</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3. Correction Curves for Stearic Acid-1-Carbon-14 Plated from Benzene Solutions. (Counts for 0.1-ml aliquots plated on chilled, 25-mm watch glasses.)
To illustrate the use of the corrections described above, data and corrections for a surface area determination are given in Table IV below, followed by the actual calculation of the surface area from the corrected data.

### TABLE IV

**DATA AND CORRECTIONS FOR SURFACE AREA OF FERRIC OXIDE**

<table>
<thead>
<tr>
<th></th>
<th>Initial Solution</th>
<th>Final Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counts corrected for dead time</td>
<td>5357</td>
<td>4830</td>
</tr>
<tr>
<td>Counts corrected for tube response (X 3931/3172)</td>
<td>6639</td>
<td>5986</td>
</tr>
<tr>
<td>Concentration read from correction curve</td>
<td>4.14 gm/liter</td>
<td>3.71 gm/liter</td>
</tr>
</tbody>
</table>

*a* Sample No. 46 in Table V; sample weight, 0.1838 gm; $S_w$ by BET = 10.1 m$^2$/gm.

Calculations from above data:

$$S_w = \left(\frac{0.00414 \text{ gm/ml} - 0.00371 \text{ gm/ml}}{284.47 \text{ gm/mole x 0.1838 gm}}\right) \times \frac{10 \text{ ml}}{0.023 x 20.5 \times 10^{-20} \text{ m}^2/\text{mole}}$$

$$= 10.15 \text{ m}^2/\text{gm}.$$

### E. General Method for Surface Area Determination by Radiostearic Acid Sorption

Several variations of the technique for surface area determination described in Section III B were investigated. By the utilization of numerous powders of known specific surface area (determined by the BET nitrogen adsorption method in the course of this project or during earlier studies), experiments were conducted in which type of sample bottle, temperature, solution concentration, specific activity of radiostearic acid, and sample weight were varied. In the technique eventually adopted for general use, powders were predried by heating at least one hour at 110°C. Samples were then weighed, by difference, into 4-ounce wide-mouthed sample bottles with screw caps and Teflon cap liners, heated 6 hours in a vacuum oven at 110°C and 20 to 25 inches mercury vacuum, and cooled in a desiccator before addition of the stearic acid.
solution. After the stearic acid, usually 10 ml, had been added, the sample bottle was closed, shaken vigorously, and allowed to equilibrate one hour (with occasional shaking) in a constant-temperature water bath. The solution was then decanted from the sample bottle and centrifuged in a stoppered, 15-ml glass tube. (Lusteroid tubes were softened by the benzene and adsorbed some of the acid from these solutions.) The supernatant liquor was decanted into another tube and stoppered. Since most of the tests were made at relatively low temperatures, e.g. 14°C, the solutions were equilibrated at room temperature before aliquots were plated. (Plating of the chilled solution in the water bath was rejected because it increased the possibility of carbon-14 contamination in the laboratory.) The 0.1-ml aliquots were plated on chilled watch glasses and counted in the manner described in previous sections of this report. Data from these surface area determinations are presented in Table V except for those for clay samples, which are all compiled in Table I.

Several early experiments had indicated that for some powders, notably clays and nickel, the adsorption of either moisture or air during the removal of dried samples from vacuum oven to desiccator affected stearic acid sorption adversely. Therefore, a special round-bottom sample flask was constructed for use with such samples. With a stopcock above the ground-glass joint in its neck, this flask can be attached to a vacuum pump and evacuated while it is being heated in a Glas-Col heating mantle. After 6 hours of drying and degassing at 120°C, samples in this flask are protected from contact with moisture in the air by closing the stopcock and attaching to it a burette filled with radiostearic acid solution. The desired volume of solution can then be added to the sample without admitting air to the system. Determinations in which this flask has been used are indicated in Table I and V.

To facilitate the choice of sample size and solution volume in surface area determinations, the quantity of acid which would be sorbed per gram of powder was listed for several different surface areas and is presented here in Table VI. The solubility data given below in Table VII were plotted on log-log paper for determination of the maximum concentrations of stearic acid in benzene appropriate for use at the desired temperatures.
<table>
<thead>
<tr>
<th>No.</th>
<th>Sample Powder</th>
<th>$S_w$ by BET (M$^2$/Gm)</th>
<th>Sample Weight (Gm)</th>
<th>Temp. (°C)</th>
<th>Sol. Vol. (ML)</th>
<th>Initial Conc. (Gm/Liter)</th>
<th>$C/C_0$</th>
<th>Beta Radiation Initial (Counts/Minute)</th>
<th>$S_w$ by Radiostearic Acid Sorption</th>
<th>$S_w$ by Beta Radiation Final (Counts/Minute)</th>
<th>$S_w$ (M$^2$/Gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Silica</td>
<td>98.9</td>
<td>1.8537</td>
<td>22</td>
<td>10</td>
<td>8.6</td>
<td>0.23</td>
<td>5682</td>
<td>4590</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Silica</td>
<td>98.9</td>
<td>1.0385</td>
<td>22</td>
<td>10</td>
<td>8.6</td>
<td>0.24</td>
<td>14573</td>
<td>12122</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Nickel</td>
<td>16.8</td>
<td>1.3419</td>
<td>22</td>
<td>10</td>
<td>8.6</td>
<td>0.20</td>
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<td>10237</td>
<td>8.8</td>
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<tr>
<td>14</td>
<td>Zinc</td>
<td>2.3</td>
<td>3.4430</td>
<td>22</td>
<td>10</td>
<td>10.79</td>
<td>0.34</td>
<td>17225</td>
<td>16490</td>
<td>0.6</td>
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<tr>
<td>15</td>
<td>Zinc</td>
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<td>4.0696</td>
<td>22</td>
<td>10</td>
<td>10.79</td>
<td>0.33</td>
<td>16217</td>
<td>14804</td>
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<tr>
<td>16</td>
<td>Zinc oxide</td>
<td>4.7</td>
<td>4.1635</td>
<td>22</td>
<td>15</td>
<td>10.79</td>
<td>0.26</td>
<td>17850</td>
<td>12786</td>
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<tr>
<td>17</td>
<td>Zinc oxide</td>
<td>4.7</td>
<td>1.8</td>
<td>22</td>
<td>10</td>
<td>10.79</td>
<td>0.29</td>
<td>17850</td>
<td>14297</td>
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<td>0.27</td>
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<td>4.2</td>
<td>5.2907</td>
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<td>10.79</td>
<td>1.1b</td>
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<td>15009</td>
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<td>20</td>
<td>Cupric oxide</td>
<td>4.2</td>
<td>2.0514</td>
<td>15.6</td>
<td>10</td>
<td>10.79</td>
<td>1.1b</td>
<td>17185</td>
<td>15267</td>
<td>2.5</td>
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<tr>
<td>21</td>
<td>Alumina</td>
<td>3.36</td>
<td>0.4755</td>
<td>15</td>
<td>10</td>
<td>8.15</td>
<td>1.0b</td>
<td>15444</td>
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<tr>
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<td>Ferric oxide</td>
<td>2.98</td>
<td>0.9771</td>
<td>15</td>
<td>10</td>
<td>8.15</td>
<td>1.0b</td>
<td>15444</td>
<td>14581</td>
<td>2.0</td>
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</tr>
<tr>
<td>23</td>
<td>Calcium sulfate</td>
<td>17.9</td>
<td>0.4641</td>
<td>14</td>
<td>10</td>
<td>7.61</td>
<td>0.91b</td>
<td>17350</td>
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<td>20.3</td>
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<tr>
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<td>Nickel</td>
<td>24</td>
<td>0.5769</td>
<td>14</td>
<td>10</td>
<td>7.61</td>
<td>0.80b</td>
<td>17350</td>
<td>10968</td>
<td>21.1</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>Glass beads</td>
<td>0.35</td>
<td>2.2642</td>
<td>14</td>
<td>10</td>
<td>3.43</td>
<td>0.51</td>
<td>6423</td>
<td>5792</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Titanium dioxide</td>
<td>7.7</td>
<td>0.4642</td>
<td>14</td>
<td>10</td>
<td>3.43</td>
<td>0.47</td>
<td>6423</td>
<td>5308</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>Iron</td>
<td>21.3</td>
<td>1.0423</td>
<td>14</td>
<td>10</td>
<td>3.42</td>
<td>0.57</td>
<td>9110</td>
<td>9060</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>Ferric oxide</td>
<td>4.2</td>
<td>0.6171</td>
<td>14</td>
<td>10</td>
<td>3.83</td>
<td>0.55</td>
<td>16359</td>
<td>14146</td>
<td>4.01</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>Calcium sulfate</td>
<td>17.9</td>
<td>0.3464</td>
<td>14</td>
<td>10</td>
<td>3.83</td>
<td>0.61</td>
<td>16359</td>
<td>15989</td>
<td>4.24</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Zinc carbonate</td>
<td>4.9</td>
<td>1.8653</td>
<td>13</td>
<td>20</td>
<td>1.67</td>
<td>0.10</td>
<td>14503</td>
<td>4164</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>Zinc oxide</td>
<td>6.1</td>
<td>4.2943</td>
<td>14</td>
<td>20</td>
<td>3.52</td>
<td>0.08</td>
<td>15042</td>
<td>1917</td>
<td>6.3</td>
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<tr>
<td>32</td>
<td>Nickel</td>
<td>16.8</td>
<td>0.3871</td>
<td>14</td>
<td>10</td>
<td>3.35</td>
<td>0.47</td>
<td>13770</td>
<td>11682</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>Silica</td>
<td>91</td>
<td>0.4978</td>
<td>29</td>
<td>10</td>
<td>36.5</td>
<td>0.25</td>
<td>3290c</td>
<td>2928d</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>Molecular sieve, 5A</td>
<td>688</td>
<td>0.4624</td>
<td>29</td>
<td>70</td>
<td>29.7</td>
<td>0.33</td>
<td>13791</td>
<td>13041</td>
<td>485</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>Ferric oxide</td>
<td>10.1</td>
<td>0.3418</td>
<td>14</td>
<td>10</td>
<td>3.297</td>
<td>0.63</td>
<td>4903</td>
<td>4573</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>Manganese dioxide</td>
<td>44.8</td>
<td>0.1923</td>
<td>14</td>
<td>12</td>
<td>3.297</td>
<td>0.65</td>
<td>4990</td>
<td>4798</td>
<td>4.24</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE V (Continued)

**SPECIFIC SURFACE AREA ($S_w$) DETERMINATIONS: OXIDES, METALS, SALTS, AND GLASS**

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample Powder</th>
<th>$S_w$ by BET (M$^2$/Gm)</th>
<th>Sample Weight (Gm)</th>
<th>Temp. (°C)</th>
<th>Sol. Vol. (ML)</th>
<th>Initial Conc. (Gm/Liter)</th>
<th>$C/C_0$</th>
<th>Beta Radiation Initial (Counts/Minute)</th>
<th>$S_w$ (M$^2$/Gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>Manganese chloride</td>
<td>5.77</td>
<td>0.5907</td>
<td>14</td>
<td>10</td>
<td>3.927</td>
<td>0.61</td>
<td>4990</td>
<td>4460</td>
</tr>
<tr>
<td></td>
<td>Ferric oxide</td>
<td>10.1</td>
<td>0.1838</td>
<td>14</td>
<td>10</td>
<td>3.927</td>
<td>0.59</td>
<td>5267</td>
<td>4759</td>
</tr>
<tr>
<td></td>
<td>Manganese dioxide</td>
<td>44.8</td>
<td>0.0907</td>
<td>14</td>
<td>10</td>
<td>3.927</td>
<td>0.48</td>
<td>5010</td>
<td>3676</td>
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<td></td>
<td>Nickel (5)</td>
<td>16.8</td>
<td>0.1234</td>
<td>14</td>
<td>10</td>
<td>3.927</td>
<td>0.46</td>
<td>5172</td>
<td>3660</td>
</tr>
<tr>
<td>49</td>
<td>Manganese chloride</td>
<td>5.77</td>
<td>0.5142</td>
<td>14</td>
<td>10</td>
<td>4.70</td>
<td>0.64</td>
<td>7440</td>
<td>6091</td>
</tr>
<tr>
<td></td>
<td>Nickel (5)</td>
<td>16.8</td>
<td>0.1562</td>
<td>14</td>
<td>10</td>
<td>4.03</td>
<td>0.60</td>
<td>6375</td>
<td>5707</td>
</tr>
<tr>
<td>50</td>
<td>Alumina</td>
<td>3.36</td>
<td>0.2684</td>
<td>14</td>
<td>10</td>
<td>4.70</td>
<td>0.71</td>
<td>7440</td>
<td>6777</td>
</tr>
<tr>
<td>52</td>
<td>Nickel</td>
<td>3.36</td>
<td>0.2684</td>
<td>14</td>
<td>10</td>
<td>4.03</td>
<td>0.60</td>
<td>6375</td>
<td>5707</td>
</tr>
</tbody>
</table>

- $C/C_0 = \text{final concentration/saturation concentration}$.
- These high $C/C_0$ values were possible because the solutions were made up and the powders were added to them at room temperature. Thus enough sorption occurred before the samples were put in the cold water bath to prevent precipitation of stearic acid upon cooling.
- Before plating, 0.6 ml was diluted to 4.6 ml.
- Before plating, 1 ml was diluted to 5 ml.
- Sample was heated and evacuated in special sample flask described in Section III E.
- Because of iced-in weather conditions, work was halted for several days, and this powder remained in the stearic acid solution 7 days. The very high surface area obtained indicates a chemical reaction.
TABLE VI
AID FOR ESTIMATING VOLUME OF FATTY ACID SOLUTIONS
REQUIRED FOR SURFACE AREA DETERMINATIONS

<table>
<thead>
<tr>
<th>Approximate Surface Area of Powder (m²/Gm)</th>
<th>Fatty Acids Sorbed by Powder (Moles x 10⁴/Gm)</th>
<th>Stearic Acid Sorbed by Powder (Gm/Gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.081</td>
<td>0.0023</td>
</tr>
<tr>
<td>5</td>
<td>0.404</td>
<td>0.0115</td>
</tr>
<tr>
<td>10</td>
<td>0.808</td>
<td>0.0230</td>
</tr>
<tr>
<td>15</td>
<td>1.212</td>
<td>0.0345</td>
</tr>
<tr>
<td>20</td>
<td>1.616</td>
<td>0.0460</td>
</tr>
<tr>
<td>25</td>
<td>2.020</td>
<td>0.0575</td>
</tr>
<tr>
<td>30</td>
<td>2.424</td>
<td>0.0690</td>
</tr>
<tr>
<td>40</td>
<td>3.232</td>
<td>0.0920</td>
</tr>
<tr>
<td>50</td>
<td>4.040</td>
<td>0.1150</td>
</tr>
<tr>
<td>75</td>
<td>6.060</td>
<td>0.1725</td>
</tr>
<tr>
<td>100</td>
<td>8.080</td>
<td>0.2300</td>
</tr>
</tbody>
</table>

TABLE VII
SOLUBILITY OF STEARIC ACID IN GRAMS
PER 100 GRAMS OF SOLVENT

<table>
<thead>
<tr>
<th>Solvent</th>
<th>10°C</th>
<th>20°C</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.24</td>
<td>2.46</td>
<td>12.4</td>
<td>51.0</td>
<td>145</td>
<td>468</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.20</td>
<td>2.4</td>
<td>10.5</td>
<td>43.8</td>
<td>133</td>
<td>450</td>
</tr>
<tr>
<td>Methanol</td>
<td>----</td>
<td>0.1</td>
<td>1.8</td>
<td>11.7</td>
<td>78</td>
<td>520</td>
</tr>
</tbody>
</table>

IV. DISCUSSION AND CONCLUSIONS

A. Materials and Apparatus

1. Dry Box

Because the manipulation of pipettes and burettes inside the dry box was difficult, the precision of measurements made in the box was doubtful. High accuracy is required in the measurement of sorbate solution into sample bottles and in sample plating, thus these procedures were transferred from the dry box to a laboratory bench covered with a large, protective sheet of blotting paper. By localizing to this area all steps in which stock solutions were measured, sample bottles were opened, solutions were transferred, etc., laboratory contamination was kept to a minimum.

2. Counters

The end-window Geiger tubes were found to be adequate for counting stearic acid-1-carbon-14 at the specific activities used in this project. A dip type of counter was considered for counting the solutions of stearic acid and thus avoiding the necessity of precise plating. Use of such a counter did not seem advisable, however, since the counter itself might sorb as much as 0.3 of a monolayer of stearic acid on its surface.20

3. Stearic Acid Solutions

Due to the discrepancy between BET and radiostearic acid surface area values for some of the powders, some consideration was given to the possibility of self-decomposition of radiostearic acid. However, according to Tolbert,21 the radiation-induced self-decomposition of stearic acid-1-carbon-14 would be negligible at the concentrations and specific activities used in this project. In addition, private communications from Tracerlab22

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22 M. A. Stolberg, Head, Chemistry Dept., Tracerlab, Inc., Waltham 54, Mass.
and Volk Radiochemical Co.\textsuperscript{23} state that they have had no evidence of self-decomposition in this compound at specific activities as high as 2 milli-curies per millimole and stored at least one year.

B. Preliminary Experiments

The preliminary experiments indicated several refinements necessary to make radioassay of sorbed stearic acid a practical and relatively fast method of determining the specific surface area of powders. For example, at room temperature a $C/C_o$ value as high as 0.3, which is desired because one surface area determination at this concentration ratio should be adequate for most powders and should obviate the determination of isotherms for each powder tested, requires a high concentration of stearic acid in benzene (greater than 14 grams per liter at $25^\circ$ C). The result is that the acid sorbed by a low-surface powder, even at the highest ratio of sample weight to sorbate solution that can be adequately mixed (usually about 4 grams per 10 ml, depending on the powder density), is a very small fraction of the total acid in the solution. In radioassay of the initial and final concentrations, the sorbed acid is then represented by a small difference between large numbers. (In some cases, the difference between $C$ and $C_i$ was no greater than the probable random error in counting.) Since the solubility of stearic acid in benzene decreases sharply as the temperature is lowered (see Table VII), the sorption temperature for these determinations was reduced to $14^\circ$ or $15^\circ$ C. As can be seen in Table V, high values of $C/C_o$ are possible in tests run at these temperatures. Early experiments also indicated that for some powders, especially clays, either moisture from the air or the air itself adsorbed by the powder during its transfer from vacuum oven to desiccator interfered with sorption of stearic acid. Also disclosed by preliminary work were the importance of precision plating and the need to modify the calculation of surface area given by equation (1), p. 8, to take into account the effects of self-absorption on quantitative interpretation of data.

C. Plating Techniques

Because of the short range of "soft" beta radiation such as is emitted by carbon-14, duplication of size, thickness, and shape in preparing plates

\textsuperscript{23}M. E. Volk, President, Volk Radiochemical Company, Chicago 40, Illinois.
for radioassay is of paramount importance. When identical volumes of a benzene-stearic acid are plated on various surfaces, many variations in size, shape, deposit uniformity and thickness may result. Due to the volatility of benzene, the ambient temperature and the speed of ejection from pipette or syringe affect the form taken by the stearic acid deposit. The cleanliness of a solid substrate and the surface tension of a liquid substrate also influence the shape and the extent to which the solid builds up a thick ridge at the periphery of the deposit. Nitrobenzene in a watch glass was found to be a good substrate, evidently because of its particular combination of the following properties: relatively high surface tension, high density, miscibility with the benzene-stearic acid solutions, and low solvation power for stearic acid. Nitrobenzene was rejected for general use, however, because its high boiling point results in a liquid layer that remains under the deposited acid for several days and hampers the handling of plated samples. (The plates cannot be heated to evaporate the solvent because losses of stearic acid would probably be incurred.) Plating 0.1-ml aliquots onto chilled 25-mm watch glasses with subsequent transfer to the refrigerator for slow evaporation was incorporated into the radiostearic acid determinations of surface area. Results with this plating technique have been fairly consistent, with average deviations usually under 2 per cent and often under one per cent.

D. Corrections Applied to Counting Data

Corrections for tube dead time should be made when working with specific activities as high as those used in this investigation. In addition, tube response should be checked at each counting session to validate comparisons of data taken at different times. The empirical corrections described in Section III D are important, even at concentrations as low as 2 grams per liter. At this concentration and with a specific activity of 0.246 milli-curies per gram, was found a loss of approximately 18 per cent of the count expected in direct ratio to counts obtained for a concentration of 0.5 gram per liter with the same specific activity. There are several factors that may combine to prevent the count from 0.1 ml at a concentration of 2 grams per liter from being four times as large as the count from 0.1 ml at 0.5-gram-per-liter concentration. The largest contributor to this discrepancy
may be self-absorption, which increases with increasing concentration. The difference in deposit diameter obtained from 0.1-ml plates of different concentrations is also a factor, as is back-scatter of the radiations. The latter effect would tend to make counts larger than expected, especially at the lower concentrations. The empirical method developed to correct for these influences seems to be adequate, particularly for concentrations on the straight segments of the curves shown in Figure 3.

E. General Method for Surface Area Determination by Radiostearic Acid Sorption

The general method for surface area determination described in Section III E has been found applicable to a number of powders of low and moderate surface area, including zinc oxide, for which results have been quite consistent, alumina, ferric oxide, nickel, zinc carbonate, manganese dioxide, manganous chloride, zinc, cupric oxide, titanium dioxide, and clays. Some values which vary with the BET determinations by as much as 25 per cent, e.g. 7.7 vs 5.6 m²/gm for titanium dioxide, are considered to be fair checks, since surface areas obtained by the BET method may be as much as 15 per cent inaccurate at this low range. A judicial combination of sample weight, stearic acid concentration, solution volume, and temperature is necessary to obtain accurate results. By using the information in Tables VI and VII, one should be able to plan successful determinations of most powders, excluding those of high porosity. Even though a porous sample such as molecular sieve may have pores large enough to admit stearic acid molecules, the long acid chains may fill the pores and block entrances to them before all the sites on the inner surfaces are filled. In other cases the pores, or entrances to them, may be too small to accommodate stearic acid molecules.

When a series of samples to be tested have a rather narrow range of surface area, e.g. 10 to 30 m²/gm, the same experimental conditions can be used for each determination. If, however, the surface areas of the unknowns may vary from 0.1 to 100, different weights and/or stearic acid concentrations must be used for the opposite extremes. In general, a determination can be made on a one-gram sample at 15°C with 10 ml of stearic acid having a concentration of 7-8 grams per liter and a specific activity of 0.1-0.2 millicurie per gram of acid. Vacuum-oven drying of samples in wide-mouthed sample bottles with Teflon-lined screw tops has been found adequate for some samples, parti-
cularly for zinc oxide, which seems to be fairly insensitive to moisture. At high humidities, however, moisture reaching the dried sample when it is removed from the vacuum oven and capped can lower the surface area value by occupying the surface and preventing formation of a stearic acid monolayer. In other cases, according to Hirst and Lancaster,\textsuperscript{24, 25} it can raise the surface area above its true value by promoting chemical reaction of the powder and stearic acid. To prevent the admission of moisture to the dried sample, the flask with stopcock described in Section III E should be used. Several of these can be simultaneously evacuated by attaching them to a multibranched glass tube leading to the vacuum pump.

When a sample run at the conditions suggested above gives a very low surface area (less than 5 square meters per gram), the determination should be repeated at 14° C with a concentration of approximately 4 grams per liter and a sample weight of 2 grams. On the other hand, if the unknown is found to have a rather high surface area and its determination results in a C/C\textsubscript{o} value considerably under 0.3, it should be rerun with a smaller powder sample, e.g., 0.1 gram. If the two determinations do not agree, the latter one in each of the above cases should be the more reliable.

This method could be developed for routine use and is not as tedious as the BET nitrogen adsorption method. By drying and equilibrating six samples at once to reduce the proportion of drying time to total time, the average time per sample would be about 2-1/2 hours, including one 3-minute count for each of three replicate plates made for the initial and final concentrations. The time can be reduced by degassing powders at higher temperatures if there is no danger of their decomposition.

\textsuperscript{24}W. Hirst and J. K. Lancaster, \textit{loc. cit.}

V. SUMMARY

In this investigation, undertaken to develop a method for surface area determination by sorption of fatty acids labelled with a radiotracer, solutions of stearic acid-1-carbon-14 in benzene were used. Since the size and shape of plated samples are so critical in obtaining reproducible counts of the low-energy beta radiation emitted by carbon-14, considerable time was spent in experimenting with plating techniques. One that gave consistently good results and was adopted for general use consisted of pipetting 0.1-ml aliquots on to chilled, 25-mm watch glasses and returning them to the refrigerator for slow solvent evaporation.

Though the conditions (sample weight, solution concentration, etc.,) must be varied somewhat for powders at the opposite extremes of the surface area range of 0.1 to 100 m²/gram, a general method for surface area determination by radioassay of stearic acid sorption has been developed. It consists of the following steps: (1) weigh approximately one gram of oven-dried powder into sample flask (preferably a 100-ml round-bottom flask with a stopcock above the ground-glass joint at the neck); (2) heat 6 hours at 110°C while simultaneously degassing by vacuum pump; (3) close stopcock, cool sample, and above the stopcock attach a burette filled with the benzene solution of radiostearic acid (7 to 8 grams/liter; 0.1-0.2 millicurie/gram of acid); (4) measure 10 ml of solution into flask, close stopcock, and shake vigorously; (5) let sample equilibrate in water bath one hour at 15°C, with occasional shaking; (6) decant the solution into a centrifuge tube stopper, and centrifuge briefly; (7) decant to another tube, stopper, and let the solution reach room temperature before plating; (8) pipette three or more 0.1-ml aliquots of this solution and of original solution to chilled, 25-mm watch glasses and place in refrigerator for slow evaporation of the benzene; and (9) count the plates with a thin end-window Geiger counter.

To improve the accuracy of these determinations, an empirical correction for self-absorption (and other factors, such as deposit diameter and back-scatter of radiation, tending to distort the relation of observed counts to solution concentration) has been developed. A standard correction curve is made by plating 0.1-ml aliquots of known concentrations of radiostearic acid (of the same specific activity as that used in the
determinations) in benzene, counting these, and plotting concentration versus counts. The concentration of the unknown solutions plated and counted can then be read from this curve and used to calculate surface area by the equation given below.

\[
S_w = \frac{(\text{initial-final}) \text{ moles/ml} \times 10 \text{ ml} \times 6.023 \times 10^{23} \times 20.5 \times 10^{-20} \text{ m}^2/\text{mole}}{\text{sample weight}}
\]
VI. FUTURE PROGRAM

It is recommended that further study be made of the problem of precision plating and counting of radiostearic acid from benzene solutions. One possibility is to plate the solution on paper that has been impregnated with a liquid scintillator, so that beta-induced scintillations are counted instead of the beta radiations themselves. It is also desirable to study the powders for which radiostearic acid sorption did not agree with BET nitrogen adsorption values and to determine whether the discrepancy was due to experimental conditions, experimental error, or some characteristic of the powder. In addition, the possibility of determining pore size by radioassay of several sorbed fatty acids with chains from 1 to 22 carbons long should be explored.

Respectfully submitted:

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