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Subject: Adsorption from Solution Methods
for Surface Area Measurement

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The principle behind all these wet adsorption methods is outlined in K-1065⁽¹⁾. The methods recently developed differ from that described therein only in the adsorbates used and the methods used for determining the solute concentration. We will therefore confine this communication to a description of the analytical procedures and steps of significant importance in obtaining reliable results.

1. The calibrating powder. We employ Coleman and Bell reagent grade CaF_2 as our standard powder. The surface area of the sample in use here is 15.85 sq.m./g. as determined by nitrogen adsorption methods. This area remains constant on storage of the powder in a desiccator; exposure to moist air may cause the surface area to decrease. The calibrating value should be close to 1 m² surface area equals 2.9 mg., 1.08 mg., and 0.87 mg. adsorbed, in the NaPFO , HPFO , and Cu(PFB)_2 methods, respectively.
2. The sodium perfluorooctanoate (NaPFO) method. Analysis depends on extracting perfluorooctanoic acid from aqueous solution into an organic solution, separating the organic extract and determining the acid by iodide-iodate titration. Details follow:
 - a. Weigh out 1-2 g. sample of powder (more if powder has much lower surface area than the standard powder). Place in 40 ml. centrifuge tube.
 - b. Add 5 ml. 0.05 N NaOH (Note 1) to wet powder thoroughly (stir with glass rod) and then add 25 ml. standard NaPFO solution. Mix well and cap with rubber stopper.

⁽¹⁾ Sutherland, J. E., Whetsel, H. B., and Mills, G. F., The Measurement of Surface Area by the Adsorption of Calcium Perfluorobutyrate, Oak Ridge Gaseous Diffusion Plant, Union Carbide Nuclear Company, Oak Ridge, Tennessee, (K-1065), October 1, 1953.

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- c. Shake for 5 minutes and centrifuge to settle powder.
- d. Take 15 ml. aliquot from clear supernate and add to separatory funnel containing 25 ml. CCl_4 -ethyl ether (9:1 by volume) solvent and add 20 ml. aqueous solution 0.2 N in H_2SO_4 and saturated with Na_2SO_4 . Shake briefly and release pressure through top stopper; then mix thoroughly by shaking for 1 minute.
- e. Allow phases to separate and remove about 24 ml. of the organic layer through the bottom stopcock. Add 25 ml. more of the organic solvent mix and extract a second time. Add the second extract to the first, again leaving about 1 ml. of solvent in the funnel.
- f. Add water, sodium iodide, and potassium iodate to the extract and titrate the iodine set free with standard thiosulfate (Note 2).

Note 1: The 0.05 N NaOH should be added first as the NaPFO forms a film on the powder which may prevent thorough wetting and access of the adsorbate to the adsorbant. The alkali also serves to neutralize any free acidity in the sample of adsorbant. If the adsorbant contains much free acid, or is a naturally acidic material, it may be necessary to use a more concentrated NaOH solution. The slurry should not be so strongly alkaline, however, that the free alkali neutralizes any large amount of the H_2SO_4 solution used in the extraction step.

Note 2: The iodide-iodate salts should not be added until just before titrating, as iodine loss may ensue. A magnetic stirrer, the Labline Magnestir type, is very useful for mixing the organic and aqueous phases in this titration. Titrate with standardized (~ 0.05 N) sodium thiosulfate until the iodine color is pale yellow before adding starch to complete the titration. The stirrer should be stopped and the starch solution added to the aqueous phase. Carried out in this way, the endpoint is very sharp.

General observations: The aqueous NaPFO solution should contain about 50-55 mg. solute per ml. It is prepared by adding aqueous NaOH to the free acid suspended in water; add a small excess of alkali (a drop or two of phenolphthalein, no more, serves as an indicator). Single area determinations require 40-60 minutes exclusive of washing glassware and preparing solutions. On a routine basis, and with a full workload of samples, the time per sample can be reduced to about 30 minutes.

3. The perfluorooctanoic (HPFO) acid method. This method does not involve any extraction procedure as the acid is directly titratable. It is very rapid, only about 10 minutes being required for an individual determination; duplicate samples are unnecessary. Details follow:
 - a. Prepare the standard solution by dissolving HPFO in 10 ml. ether and adding 390 ml. CCl_4 . The solution should contain about 10 mg. HPFO/ml. final solvent mixture.

- b. To 1.0-2.0 g. dry powder in 40 ml. centrifuge tube, add 25 ml. standard HPFO solution and stir with glass rod about 30 seconds.
 - c. Cap with rubber stopper and centrifuge to settle powder.
 - d. Take 15 ml. aliquot from clear supernate, add water, sodium iodide, and potassium iodate. Titrate as before with good stirring using 0.025 N. sodium thiosulfate.
4. The copper perfluorobutyrate ($\text{Cu}(\text{PFB})_2$) method. This is also a rapid method as no extractions are involved. Proceed as follows:
- a. Prepare standard solution of $\text{Cu}(\text{PFB})_2$ (Note 1) by dissolving 6.0 g. of the salt in 40 ml. ethylether and adding to this solution a mixture of 270 ml. CCl_4 and 20 ml. ethyl ether. Let stand 1 hour and filter off any precipitate which forms. Use 23 cm. fluted paper filter and filter by gravity only; cover filter with cover glass to prevent excessive evaporation of solvent. The solution is stable only for one day. Use good quality cork stopper in standard solution bottle.
 - b. To 1.0-2.0 g. dry powder in 40 ml. centrifuge tube add 20 ml. std. solution and stir with glass rod for about 30 seconds.
 - c. Cap with rubber stopper and centrifuge to settle powder.
 - d. Take 10 ml. aliquot from clear supernate, add sodium iodide and water. Titrate with good stirring using 0.025 N. sodium thiosulfate. This end point is slow; allow 1 minute to be sure it is complete.
 - e. Some copper may be removed by chemical reaction with adsorbed acids on the powder. If so, an equivalent amount of free fluorobutyric (HPFB) acid is formed in solution. This can be tested for by adding KIO_3 to the titration mixture following step (d); more iodine forms if acid is present. Two ml. of titre in this step is equal to 1 ml. in step (d). Add one-half the amount of titre in step (e) to the amount found in (d) to get the true final concentration of $\text{Cu}(\text{PFB})_2$ and its acid equivalent.

Note 1: Prepare $\text{Cu}(\text{PFB})_2$ as follows: To 50 g. CuCO_3 (an excess), add 50 ml. water and 75 ml. perfluorobutyric acid. Warm to 50-60°C. for about 2 hours with occasional stirring. Filter under gravity through # 42 paper. This is a slow operation and can be allowed to take place overnight. Place filtrate in large crystallizing dish (or dishes) to depth of about 1/4" and evaporate at 120°C. in oven with occasional stirring to break up crust and large lumps (crush these). Keep product in desiccator.

5. General comment. The calculation of surface area in all these cases is the same and utilizes the formula below:

$$\frac{(\text{orig. conc. (mg/ml)} \times \text{vol.}) - (\text{final conc. (mg/ml)} \times \text{vol.} \times \text{aliquot factor})}{\text{conversion factor (mg/m}^2\text{)} \times \text{sample wt. in g.}}$$

equals surface area in m^2/g .

The foregoing methods will apply to many inorganic adsorbants. It will be obvious that the methods cannot be employed with materials which are appreciably soluble in the solvents used. If the adsorbant is microporous, these methods will give surface areas different from that obtained by nitrogen adsorption. This is due to the fact that areas accessible to N_2 may not be accessible to the larger organic adsorbates here employed. This difference in apparent area may be informative as to inherent porosity of the adsorbent or to the progress of aggregation of particles e.g. in slurries. While we have used CaF_2 as an illustrative standard, others could be employed as well, the standard being used to check out the method and train the operator.

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