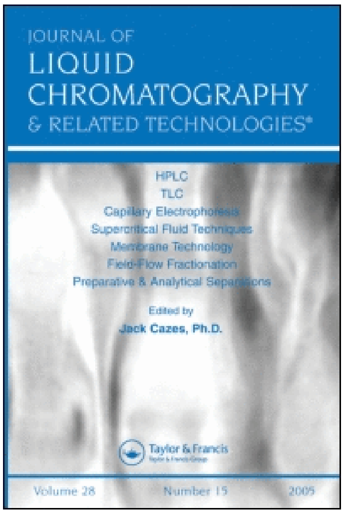

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I. Wouters[a]; I. Quintens[a]; E. Roets[a]; J. Hoogmartens[a]
[a] Katholieke Universiteit Leuven Instituut voor Farmaceutische Wetenschappen Laboratorium voo Farmaceutische Chemie Van Evenstraat, Leuven, Belgium

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CORRELATION BETWEEN SPECIFIC SURFACE AREA AND METHYL RED ADSORBED ON SILICA GEL

I. WOUTERS, I. QUINTENS, E. ROETS, AND J. HOOGMARTENS
Katholieke Universiteit Leuven
Instituut voor Farmaceutische Wetenschappen
Laboratorium voo Farmaceutische Chemie
Van Evenstraat 4
B-3000 Leuven, Belgium

ABSTRACT

The amount of methyl red, adsorbed on bare silica gel, has been determined for 32 samples having a specific surface area ranging from 10 m^2/g to 500 m^2/g, as determined by a BET method. A linear relationship between amount of dye adsorbed and specific area exists up to about 300 m^2/g. Beyond this value the amount of adsorbed dye does not increase correspondingly, which is believed to be due to the relative increase of micropores in the silica gel structure. It is proposed that the easily performed determination of the adsorbed methyl red can serve to estimate that part of the silica gel surface which is available for chromatographic interactions.

INTRODUCTION

The use of methyl red adsorption for surface area measurements of silica gel was first mentioned by Shapiro and

Kolthoff (1). More recently we described in detail a modified version of the original method, allowing the quantitative determination by spectrophotometry at 494 nm of the amount of methyl red adsorbed on reversed-phase materials for chromatography (2). The amount of methyl red adsorbed (mg/g), called the methyl red adsorption value (MRAV), was used as a measure for the degree of coverage of these reversed-phase materials for liquid chromatography (3,4). Adsorption of methyl red also has been used to characterize gas-liquid chromatographic packings (5). Now we used the previously described method to determine the MRAV (mg/g) of 32 underivatized, bare silica gels, obtained from 11 different sources. The results are compared with BET results.

MATERIALS

The silica gel samples analyzed are mentioned in Table 1. They were obtained from Alltech Europe (Eke, Belgium); Du Pont (Wilmington, DE, USA); Jasco (Tokyo, Japan); Macherey-Nagel (Düren, FRG); Merck (Darmstadt, FRG); Phase Separations (Queensferry, UK); Shandon (Cheshire, UK); Toyo Soda (Tokyo, Japan); Waters Associates (Milford, MA, USA); Whatman (Maidstone, UK); Dr Nondek (Prague, Czechoslovakia). The samples were collected in 1981 and 1982. The reagents for MRAV determination were of the same quality and composition as previously described (2).

A methyl red stock solution was prepared as follows. Weigh accurately about 400.0 mg of purified methyl red, dried for 2 hours at 120 °C, dissolve in dry benzene and adjust to a final volume of 100.0 ml with the same solvent. Use an ultrasonic bath when necessary. A methanolic acetate buffer was prepared as follows. Dilute a mixture of 18 ml of NaOH 1N and 100.0 ml HOAc 1N to 500.0 ml with water (pH 4.0). Dilute 25.0 ml of this solution to 500.0 ml with methanol.

The absorbance measurements were carried out with a Philips PU 8700 spectrophotometer (Pye Unicam, Cambridge, UK). For BET measurements a simple apparatus, almost entirely built following Verzele et al., was used (6). These measurements were checked by using Quantasorb equipment (Quantachrome, Syosset, NY, USA).

METHODS

For MRAV determinations the following procedure was used. Dry the sample at 120 °C for 3 hours. Allow to cool over diphosphorous pentoxide in a dessicator. Weigh quickly and accurately about 25.0 mg of the sample in a dried tube with normalized stopper. Add immediately 5.0 ml of methyl red stock solution, shake for 2 minutes on a vortex and centrifuge for 3 minutes at 4000 rpm. Dilute 1.0 ml of the supernatant solution to 50.0 ml with methanolic acetate buffer. Prepare a blanc solution. Measure the absorbance at 494 nm, using 1 mm cells, and calculate the result as mg adsorbed methyl red per gram substrate.

RESULTS

All measurements were carried out at least twice. Mean values are given in Table 1. This table also contains specific surface area information from the manufacturer and from the literature, collected in the period when the samples were received.

TABLE 1 RESULTS

Sample	Manufac-turer[a]	Specific Surface Area (m^2/g)			Methyl Red Absorption Value (MRAV)
		Manufacturer value[b]	Literature value[c]	Own BET results	
1. Kieselgel 60 (63-200 μ m)	5	NA	NA	506	223
2. Fine SiL	3	NA	380(7)	488	242
3. Kieselgel 60 (40-63 μ m)	5	514	NA	455	236
4. RSiL (10 μ m)	1	285	550(7)	455	237
5. Kieselgel 60 H TLC	5	NA	NA	435	225
6. RSiL (10 μ m)	1	NA	550(7)	423	212
7. Partisil (40 μ m)	10	NA	NA	422	210
8. Nucleosil 50 (5 μ m)	4	NA	500(7)	413	156
9. Partisil (10 μ m)	10	NA	> 400(7) 360(8)	394	206
10. Partisil (5 μ m)	10	NA	> 400(7) 380(8)	382	215
11. Kieselgel < 0.08 mm	5	NA	NA	368	203
12. LiChrosorb Si 60 (5 μ m)	5	492	550(7) 400(8) 350-550(9)	365	208
13. TSK Gel SiL 150	5	330	NA	359	200
14. Nucleosil 100 (10 μ m)	4	NA	300(7) 420(8)	347	194
15. Nucleosil 50 (10 μ m)	4	NA	500(7)	333	178
16. Silica PREP (37-75 μ m)	9	325	NA	314	204
17. Silica SEP (37-75 μ m)	9	325	NA	291	176

18. Zorbax BP SiL (7 μ m)	2	310	300(7,8)	289	161
19. LiChrosorb Si 100 (5 μ m)	5	294	273-400(9)	289	182
20. LiChrospher Si 100 (10 μ m)	5	290	250(7)	254	156
21. LiChrosorb Si 100 (10 μ m)	5	NA	330(8) 350(9)	237	154
22. Polygosil 60 (10 μ m)	4	NA	500(7) 290(8)	234	155
23. Nondek	11	NA	NA	222	139
24. Shandon 82-5-51	7	173	NA	155	111
25. Spherisorb S 5 W	6	NA	220(7) 190(10)	154	97
26. Shandon 81-3-17	7	166	NA	152	95
27. Silica RAD PAK (10 μ m)	9	250	200(7)	152	94
28. Shandon 80-10-01	7	168	NA	147	97
29. Spherisorb S 10 W	6	NA	220(7) 190(10)	144	91
30. LiChrospher Si 500 (10 μ m)	5	55	NA	57	32
31. LiChrospher Si 1000 (10 μ m)	5	22.5	NA	16	12
32. HPLC-SORB Vydac-101 Si (30-44 μ m)	4	12	NA	10	5

NA : not available.

[a] Manufacturers : 1. Alltech Europe; 2. Du Pont; 3. Jasco; 4. Macherey-Nagel; 5. Merck; 6. Phase Separations; 7. Shandon; 8. Toyo Soda; 9. Waters Associates; 10. Whatman; 11. Dr. Nondek.

[b] From a notice accompanying the sample or from a catalogue.

[c] References are mentioned in parentheses.

The repeatability of BET measurements was checked by carrying out twelve completely independent experiments over a period of 6 days. For a mean value of 328 m^2/g, the relative standard deviation was 1.9 %. The repeatability of surface measurements using the Quantasorb equipment was checked by carrying out twelve independent determinations over a period of 4 days. The relative standard deviation was 3.3 %. The surfaces obtained with this method confirmed the BET measurements, although the values were always lower. However, the average deviation did not exceed 10 %. Detailed results, obtained with this method, are not reported. The repeatability of MRAV determinations was previously checked (2). For twelve experiments with a mean of 127 mg/g a relative standard deviation of 2.3 % was obtained. The relationship between BET measurements and MRAV is shown in figure 1.

DISCUSSION

The results in Table 1 indicate that quite often a discrepancy exists between manufacturer values for specific surface area, literature values and BET values obtained in the laboratory.

The method for determination of MRAV differs from that previously published in so far that 25.0 mg samples are taken instead of 50.0 mg samples (2). It was indeed observed that for specific surface area's above 100 m^2/g higher results were obtained when smaller samples were analysed, e.g. : the Kieselgel 60 H TLC (435 m^2/g by BET) gave a MRAV of 203 for a 50 mg sample and a MRAV of 225 for a 25 mg sample. In the first example an excess of about 2 mg methyl red per milliliter solution remains present after equilibration of the sample and the methyl red stock solution, in the second example this

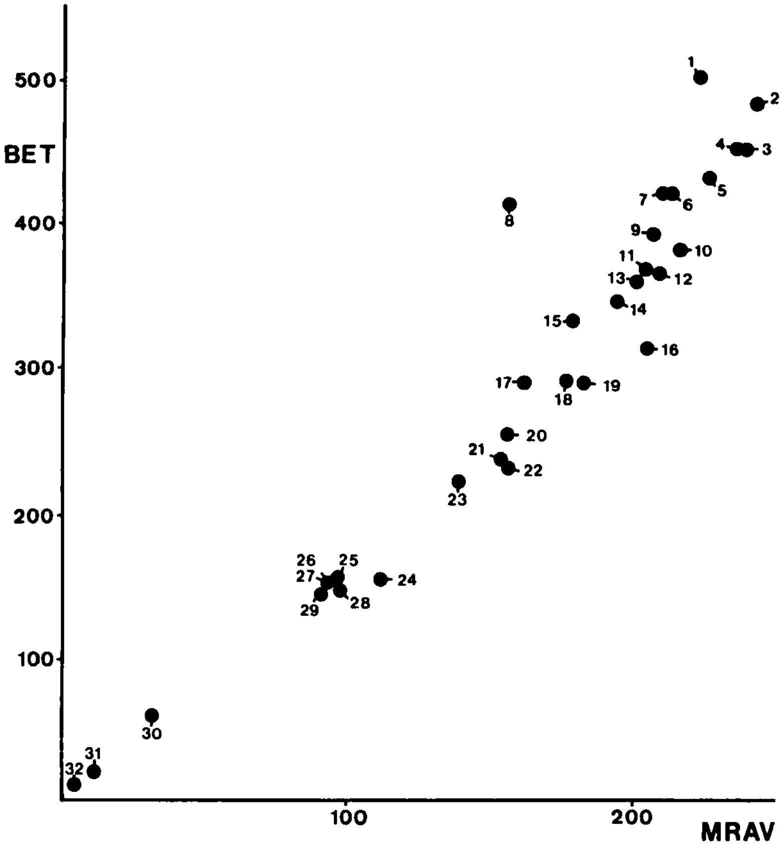

FIGURE 1. Relation between BET surface area measurements (m^2/g) and methyl red adsorption values (MRAV, mg/g).

excess is about 3 mg per milliliter. Further reduction of the sample mass gave no further increase of the MRAV, which led to the conclusion that the sample size should be reduced to 25.0 mg. The use of a more concentrated stock solution to obtain an excess of about 3 mg methyl red per millimeter was not possible due to the poor solubility of the reagent in benzene. The use of more than 5 ml of methyl red stock solution was not estimated very practical during the shaking and centrifugation manipulations.

Figure 1 shows that, although there is a clear relationship between BET and MRAV, it is linear only up to about 300 m^2/g. For samples 16 to 32 a linear correlation exists ($y = 1.60\,x - 1.0$) with a correlation coefficient of 0.92 and a standard error of estimate $S_{y,x} = 11.2$. Above 300 m^2/g the MRAV does not increase correspondingly, which is probably due to the fact that for silica gels with larger surface the relative amount of micropores increases. These micropores become more rapidly inaccessible for the larger methyl red molecule than for the small nitrogen molecule, which is used in BET experiments. Nucleosil 50 5 μ m (sample 8) is an outlier where the presence of micropores seems to play a major role. It is remarkable that sample 15, which only differs in its particle size does not show the same deviation.

The question is raised whether a larger molecule such as methyl red is not more suitable than nitrogen for the estimation of that part of the surface area of silica gel which is available for chromatographic interactions. The determination of MRAV is easy to perform and requires no special equipment.

REFERENCES

1. Shapiro, I. and Kolthoff, I.M., Studies on aging of precipitates and coprecipitation. Thermal aging of precipitated silica (silica gel), J. Org. Chem., 72, 776, 1950.

2. Wouters, I., Quintens, I., Roets, E. and Hoogmartens J., Quantitative determination of methyl red adsorption on stationary phases used in liquid chromatography, J. Liq. Chromatogr., 5, 25, 1982.

3. Wouters, I., Hendrickx, S., Roets, E., Hoogmartens, J. and Vanderhaeghe, H., Selectivity of reversed-phase packing materials in high-performace liquid chromatography of cephalosporins, J. Chromatogr., 291, 59, 1984.

4. Cachet, Th., Quintens, I., Roets, E. and Hoogmartens, J., Improved separation of erythromycin on aged reversed-phase columns, in preparation.

5. Pekov, G., Petsev, N. and Obretenova, R., Study of the absorption of methyl red on thermally treated gas-liquid chromatographic packings, J. Chromatogr., 457, 377, 1988.

6. Verzele, M., Lammens, J. and Van Roelenbosch, M., Simplified high-performace liquid chromatography phase characterization : particle size, surface area, mean pore diameter, amount of bonded phase and activity, J. Chromatogr., 186, 435, 1979.

7. Majors, R.E., Recent advances in HPLC packings and columns, J. Liq. Chromatogr., 18, 488, 1980.

8. Ohmacht, R. and Halasz, I., Eigenschaften kommerziell erwerblicher Silikagele in der schnellen Flüssigkeits - Chromatographie, Chromatographia, 14, 155, 1981.

9. Saint-Yrieix, A. and Amouroux, J., Chromatographie liquide haute performance lere partie : Fabrication de colonnes analytiques efficaces et reproductibles, Bull. Soc. Chim. France, I 225, 1982.

10. Engelhardt, H. and Müller, H., Chromatographic characterization of silica surfaces, J. Chromatogr., 218, 395, 1981.