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Note

Study of the adsorption of methyl red on thermally treated gas–liquid chromatographic packings

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A major requirement of supports for gas–liquid chromatography (GLC) is they should have low adsorption activity. Different methods for deactivation of support surfaces are used for this purpose[1]. Aue *et al.*[2] and Winterlin and Moseman[3] obtained strongly deactivated materials by heating GLC packings in an inert atmosphere at temperatures little above the maximum allowed temperature, followed by exhaustive extraction. The materials obtained are the original support coated with a chemically bound unextractable monolayer of a stationary phase, and are highly effective chromatographic supports.

Following Aue *et al.*'s idea, packings for GLC consisting of a diatomite support and various liquid stationary phases were heated at temperatures higher than the critical level for their use, and subsequently were Soxhlet extracted with the solvent used for stationary phase coating. The chromatographic retention of test solutes on the treated materials showed that they differ in the degree of deactivation from the untreated packings and the original support[4]. The deactivation depends on the initially coated liquid stationary phase. The adsorption activity of these materials, determined as described previously[5], decreases according to the chromatographic retention of different test solutes (benzene, methanol, diethyl ether, dioxane, acetone, methyl ethyl ketone, pyridine) on them, which indicates that it is possible to measure the extent of modification of GLC packings by this method easily and rapidly[6].

In this work the changes in the adsorption activity of some of these packings when heated in an oxidizing atmosphere at temperatures much above the allowed level were studied. The purpose was to establish the role of temperature and extraction in the modification process[4].

EXPERIMENTAL

Sterchamol (Schuhardt, Munich, F.R.G.), screen fraction 0.200–0.315 mm, was used as the support. The liquid stationary phases were SE-30 (BDH, Poole, U.K.) and squalane (Fluka, Buchs, Switzerland) with a 10% (w/w) coating on the packing; these two packings showed the most and the least modification effect, respectively[4]. They were heated stepwise from 100 to 1000°C for 1–4 h in air. Samples were taken after every 100°C increase and were Soxhlet extracted for 10–30 h with the solvent used for the stationary phase coating (chloroform for SE-30 and *n*-hexane for squalane). The

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TABLE I

DEPENDENCE OF METHYL RED ADSORPTION (μmol/g) ON TEMPERATURE AND TIME OF TREATMENT (HEATING AND SOXHLET EXTRACTION) OF THE SE-30–STERCHAMOL PACKING

Temperature (°C)	*Heating (h)*	*Extraction (h)*			
		0	*10*	*20*	*30*
100	1	2.13	1.03	1.01	1.14
100	2	1.11	1.09	0.95	0.94
100	4	1.11	1.01	0.94	0.95
200	2	0.98	0.82	0.74	0.76
300	2	0.61	0.51	0.47	0.47
400	2	1.42	1.41	1.40	1.42
500	2	7.40	7.42	7.42	7.41

purpose of this treatment was to follow the alterations in the stationary phases with respect to the adsorption activity of the packings until the support surface was regenerated.

The adsorption capacity of the materials studied was determined at each level of treatment by measuring the adsorption of methyl red. A sample of the adsorbent (0.2 g) was shaken with 5 ml of a 0.6 m*M* solution of methyl red in benzene; after equilibrium had been established, the solution was removed and the dye retained on the adsorbent was eluted with ethanol and measured photometrically in the suitably acidified eluate. The analytical procedure was described in detail previously[5].

RESULTS

Thermal treatment of original Sterchamol slightly influences its adsorption activity. There is only a small increase of 1.8% in methyl red adsorption up to 300°C, which is in the range of the standard error (3.5%). At higher temperatures a decrease is observed and at 1000°C the amount of dye adsorbed is 12% less than that on an

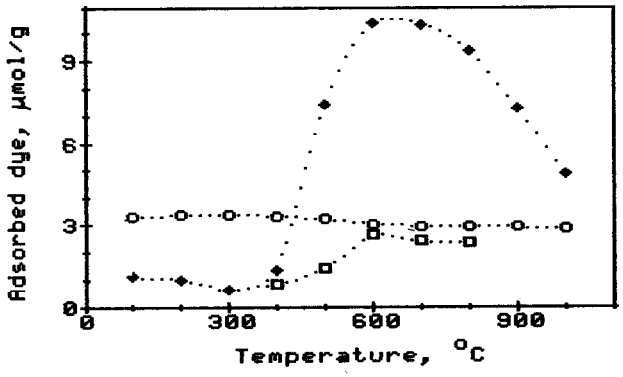

Fig. 1. Adsorption of methyl red on thermally treated (○) Sterchamol, (◆) SE-30–Sterchamol packing and (□) SE-30–Sterchamol packing Soxhlet extracted after heating at 300°C.

air-dried sample. Thermal analysis showed that Sterchamol does not undergo any definite energy transition in the studied temperature range (Fig. 3a), but from 300 to 560°C an oxidation process occurs on its surface (Fig. 3b).

SE-30–Sterchamol packing (SE-P)

The time of treatment (heating and extraction) influences the adsorption activity only at the lowest temperature. The results in Table I show that (i) heating at 100°C for more than 2 h does not change the adsorption capacity of the packing; (ii) Soxhlet extraction for more than 20 h has no influence when the sample is heated for 2 h or more; and (iii) Soxhlet extraction is not necessary for samples heated at temperatures higher than 300°C (the values in the last two columns and two lines are statistically indistinguishable).

The dependence of the SE-P adsorption activity on temperature (curve ◆) compared with that for Sterchamol (curve ○) is shown in Fig. 1. Coating the support with the stationary phase reduces its activity 3-fold. Heating this packing to 300°C leads to maximum thermal deactivation; it adsorbes 5.5 times less methyl red than Sterchamol. Extraction decreases the adsorption activity of SE-P when it is heated to this temperature but not as much as the heat treatment (Table I). Samples heated at higher temperatures show virtually no change in activity after Soxhlet extraction.

A large increase in the adsorption of methyl red occurs on further heating at higher temperature. Maximum dye adsorption is reached at *ca.* 600°C, *i.e.*, 3.5 times more than that of the support itself. The term "packing" is used conventionally because at this high temperature the material surface differs in composition and properties from those of the initial packing. This is confirmed by the fact that heat treatment up to 1000°C does not restore the adsorption capacity of the support; SE-P adsorbes 1.7 times the amount adsorbed by similarly heated Sterchamol. The adsorption surface of the support is regenerated when the initial SE-P is heated directly to 1000°C. In this instance a white amorphous substance (silica) forms on the packing surface and the solid under this white coating adsorbs to the same extent as Sterchamol heated at 1000°C (2.88 μmol/g of methyl red).

The behaviour of SE-P is different if the most deactivated sample (300°C plus extraction) is exposed to higher temperatures. The adsorption activity increases and reaches a maximum at *ca.* 600°C, but at any temperature the amount of dye adsorbed is lower than that of the support (Fig. 1, curve □).

A burn exotherm in the differential thermal analysis (DTA) curve of SE-P (Fig. 3a) begins at 380°C and ends at *ca.* 630°C, where the maximum adsorption activity of the packing occurs. The weight loss of SE-P at 630°C is 3.8% higher than that of Sterchamol at this temperature. This difference corresponds to the mass of carbon and hydrogen in the SE-30 molecule and remain unchanged up to 1000°C. The oxidation mass peak of the Sterchamol thermogravimetric analysis (TGA) curve is absent from the TGA curve of SE-P (Fig. 3b), which shows that up to 560°C the support surface is screened by the stationary phase or its decomposition products.

Squalane–Sterchamol packing (SQU-P)

The temperature dependence of the adsorption activity of SQU-P without (curve ◆) and with (curve □) extraction compared with that of Sterchamol (curve ○) is shown in Fig. 2. The heating leads to substantial modification of the packing whereas

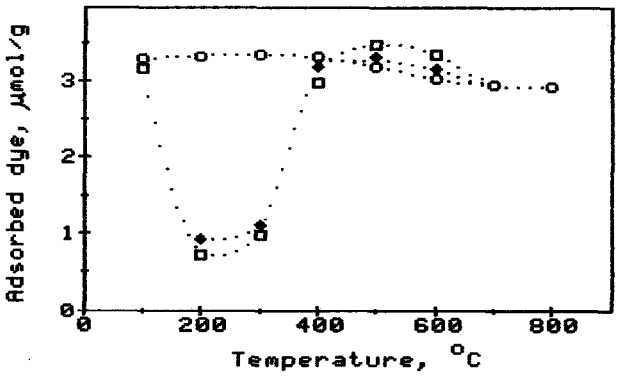

Fig. 2. Adsorption of methyl red on thermally treated (○) Sterchamol and squalane–Sterchamol packing before (◆) and after (□) Soxhlet extraction. Adsorption of methyl red on a sample heated only at 100°C cannot be measured as the squalane dissolves in benzene.

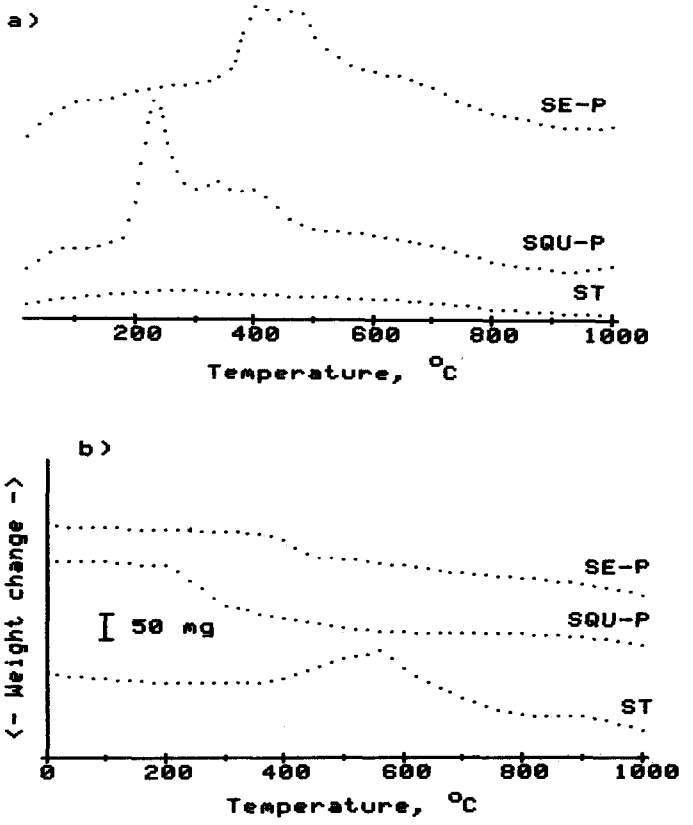

Fig. 3. (a) DTA and (b) TGA curves for Sterchamol (ST) and packings of Sterchamol with SE-30 (SE-P) and squalane (SQU-P) as stationary phases.

the extraction influences it only slightly. A SQU-P sample heated at 200°C has a 3.5-fold lower adsorption activity before extraction and a 4.7-fold lower activity after extraction than Sterchamol. This treated sample is the most deactivated of the SQU-P type; it adsorbs 0.71 μmol/g of methyl red. There is an exothermic peak in the SQU-P DTA curve at this temperature (Fig. 3a). Heating up to 500°C increases the adsorption activity of the packing, which is 2.8% higher without extraction and 8.8% higher with extraction than that of Sterchamol at this temperature. Complete regeneration of the support surface is achieved when the packing is heated up to 700°C. The weight loss of SQU-P at this temperature is 10.2% higher than that of Sterchamol and corresponds to total burning of the stationary phase. The absence of the Sterchamol oxidation mass peak from the TGA curve of SQU-P (Fig. 3b) shows that up to 560°C the support surface is blocked by some decomposition products of squalane.

DISCUSSION

The deactivation of Sterchamol by treatment at high temperatures is due to the reduction of its active surface[7]. Such treatment influences the adsorption activity of the packings studied by modifying the stationary phase. It is accepted that the liquid is retained on the support surface by adhesion forces. Depending on the subsequent heat treatment, the mode of binding of the liquid to the support and between the stationary phase can change.

Heating to 300°C deactivates the SE-P. Extraction with the stationary phase solvent does not regenerate the adsorption activity of the support but extends the deactivation process. This means that high temperatures lead to the formation of chemical bonds between the liquid and the support. At 380°C burning of SE-30 begins, which involves its organic part and linking between –Si–O–Si– chains of the SE-30 molecules becomes possible. After the organic part of the liquid has completely burnt (at *ca.* 630°C), a new surface of SE-P is formed. It is looser than that of Sterchamol and differs from it mainly in number of the active sites. Further heating of SE-P causes the same changes as for Sterchamol, *i.e.*, reduction of the active sites. The number of active groups on the packing surface is greater and the effect of deactivation is stronger than those for bare Sterchamol. When SE-P is heated directly to very high temperatures there is not enough time for linking between the stationary phase and the support to occur, and SE-30 volatilizes prior to undergoing oxidation to silica.

The temperature of maximum deactivation of SQU-P (*ca.* 200°C) is too high for squalane to be used as the stationary phase. The surface of SQU-P when heated in the range 200–300°C is hydrophobic even after extraction, in contrast to all other SQU-P samples. This means that another (different from the squalane) unextractable compound is formed on the support surface. This compound binds with the support more weakly than for SE-P and the Sterchamol adsorption capacity regenerates at *ca.* 700°C.

The most deactivated samples of the packings studied adsorb 0.47 (SE-P) and 0.71 (SQU-P) μmol/g of methyl red. These values are comparable to the adsorption of methyl red (less than 1 μmol/g) on some firm silanized diatomite supports[6]. This indicates that the treatment of the GLC packings studied leads to blockage of the active sites of the support with the stationary phase or its decomposition products, which could be as effective as silanization.

CONCLUSIONS

Thermal treatment of GLC packings with SE-30 or squalane as the stationary phase decreases the adsorption activity if the heating is carried out near to (for SE-30) or higher than (for SQU-P) the corresponding maximum allowed operating temperature. To achieve this effect it is not necessary to carry out the heating in an inert atmosphere. The deactivation is due to chemical changes in the stationary phase which binds to the support surface. Packings deactivated in this manner could serve as effective chromatographic supports.

The usual conditioning of GLC columns improves their properties not only by removing the undesirable lower boiling compounds, but also by reducing the adsorption activity of the packing at the moderate temperatures applied.

By measuring the adsorption of methyl red, it is possible to control the modification process in order to find the optimal conditions for support/packing deactivation and for support regeneration by heat treatment. Not only the temperature but also the method of heating (stepwise or direct) have a considerable effect on the results, whether the support is regenerated from the GLC packing or not.

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