Activation and Standardization of Purified Silica Gel for Column Chromatographic Cleanup of Pesticide Residue Extracts[1]

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The introduction of high purity grades of silica gel for column chromatographic cleanup procedures made available effective adsorbents for pesticide residue analysis. These adsorbents have been used for separating pesticides from interfering biological materials (2, 3, 4). However, the need still exists for a general method of reactivating and standardizing silica gel so that its activity can be consistently reproduced.

The objective of the present investigation is to determine the conditions necessary for reactivating the purified silica gel to a satisfactory degree for cleanup of pesticide residue extracts.

Materials and Methods

Reagents and Equipment. All reagents and equipment were the same as previously described (2, 3, 4) with the addition of a muffle furnace

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for reactivating the silica gel. The furnace, of a heavy box construction, was electrically heated with a powerstat control.

Procedure. Different lots of high purity silica gel grade 950 (60-200 mesh) and 923 (100-200 mesh) were used as received without heat treatment as controls. A 100-gm portion of each lot was weighed out for heat treatment and placed in a shallow porcelain evaporating dish. The furnace was pre-set at the desired temperature. The silica gel in the porcelain dish was positioned in the middle of the furnace with the thermocouple junction directly above it. Heat treatments were conducted at 130°C, 300°C, and 650°C for 2- and 24-hr periods. Upon completion of heating, the sample was put in a desiccator to cool.

In all cases activation was measured by the microcolumn cleanup method (2) as a function of rate of elution of aldrin, dieldrin and retention of a combined pool of evaporated extractives from plants, fish, mice and soil. Hexane and 40% benzene in hexane were used as eluting solvents for aldrin and dieldrin, respectively.

Results and Discussion

Different lots of adsorbent do not always yield the same results when used for the cleanup of tissue extracts by liquid-solid chromatography. This variation in lots of adsorbent can be attributed to their origin or minor differences in processing or activation methods. Reactivation and standardization studies were conducted to prepare an effective silica gel for sample cleanup.

The activation treatment described here was found to be more effective at 130°C and 300°C than at 650°C (Tables I and II). Percent recovery of aldrin and dieldrin was the criterion of silica gel activity. Low recovery of aldrin and dieldrin demonstrates high adsorption capacity of the adsorbent and vice versa. In preliminary experiments using 60% benzene in hexane to elute dieldrin, high recovery of dieldrin resulted. This made it difficult to evaluate the effect of heat treatment on the adsorption capacity of the silica gel which was also poorly demonstrated by results with aldrin (Tables I and II). However, 40% benzene in hexane, which gave partial recovery of dieldrin, demonstrated more effectively the higher adsorption capacity of silica gel heated at 130°C and 300°C compared to that obtained from the control and 650°C heat treatment (Tables I and II). There was no significant difference between 130°C and 300°C heat treatment. Two- and 24-hr heat treatment gave practically the same results in all cases. The adsorption capacity of silica gel was decreased sharply by the 650°C heat treatment as indicated from high percentage dieldrin recovery which was similar to that of control. Such results could indicate that structural changes had occurred by increasing temperature to 650°C.

Milligan and Rachford (6), in their sorption-desorption hysteresis study, pointed out that heat treatment of silica gel at a temperature around 200°C actually increases the available surface area slightly and that additional heat treatment at more elevated temperature decreases the available surface in a regular manner. It is apparent that the results reported herein might be explained by the Milligan and Rachford work.

To ascertain the activity of the adsorbent, a combined pool of pesticide extractive from plant, fish, mice and soil was used to charge the microcolumns. Subsequent elutions were made using 60% benzene in hexane for dieldrin and different solvents for other pesticides, as described in the microcolumn cleanup method (2). Adsorption of fats, waxes and pigments near the top of the microcolumn throughout the elution period indicated the high adsorption capacity of the silica gel. Treatment at 130°C and 300°C was found to be the most effective for activation of silica gel for cleanup of pesticide residues from biological material with complete recovery of pesticides. This was also indicated by the minimum background encountered in gas chromatographic determination of pesticide residues. Although high recovery of pesticides was obtained using silica gel activated at 650°C, the interfering biological material was eluted slowly off the column to the filtrate which gave high background in gas chromatographic analysis. Less interference in the analysis was noticed in the control eluate compared to that obtained from silica gel activated at 650°C. After 130°C or 300°C heat treatment of silica gel, the biological material was adsorbed and remained near the top of the microcolumn throughout the complete elution of pesticides from different lots of silica gel which gave variable results before activation. Silica gel was maintained at satisfactory activity for 60 days by keeping it in air tight containers. Two-hour heat treatment was sufficient for uniform activation of the particles throughout the layer of silica gel which was spread thinly in the shallow porcelain dish.

Heat treatment at 650°C resulted in low adsorption capacity. Bartell et al. (1), in their study of the interrelation of water content, temperature and time of activation, concluded that the water present in the gel before activation was held in two different ways. Part of the water was in comparatively large capillary spaces; the remainder was called "bound water" and was held in fine, capillary spaces. Gentle activation treatment easily removed the water filling the larger capillary pores, thereby increasing the internal surface area and activity of the silica gel. At the higher temperature the "bound water" in the fine capillary pores was removed, and the gel structure seemed to partially collapse, decreasing the internal volume (i.e., the effective surface) and the activity of the gel. Malanchuk and Stuart (5) reported that the fine-pored gel loses its porosity at about 1000°C, thus greatly decreasing the activity of the product. The high adsorption capacity of silica gel at 130°C and 300°C reported herein, indicated removal of the water in the larger capillary pores. However, treatment at 650°C led to partial collapse of the silica gel, with decreasing the effective surface area and low adsorption capacity.

Results from these experiments should be helpful for standardizing silica gel for pesticide residue analysis.

Summary

Activation and standardization studies have been conducted with high purity grades 950 and 923 silica gel to obtain an effective

adsorbent for cleanup of pesticide residue extracts. Activation of silica gel at 130°C or 300°C for a 2-hr period was very satisfactory for separating pesticides from biological materials with high recovery of pesticides. No gain in the activity of the adsorbent resulted from prolonging heat treatment beyond the 2-hr period. It was also found that the activity of the silica gel was not affected by storing it in an air-tight container for as long as 60 days.

References

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TABLE I

Percent recovery of aldrin and dieldrin from microcolumn packed with 1 gram of silica gel subjected to 24-hour treatment at different temperatures[a]

Days after treatment	Silica gel															
	Grade 950 (60-200 mesh)								Grade 923 (100-200 mesh)							
	Aldrin				Dieldrin				Aldrin				Dieldrin			
	Temperature (°C)															
	Control[b]	130	300	650	Control	130	300	650	Control	130	300	650	Control	130	300	650
1	98±3[c]	92±3	90±2	100±1	80±3	19±2	23±3	83±2	96±2	90±2	91±1	98±2	74±2	18±3	22±4	78±3
5	98±4	91±4	92±3	99±3	81±5	20±3	23±4	88±3	95±3	92±1	90±2	99±2	75±3	18±3	21±2	77±3
10	99±4	91±2	94±2	97±2	84±4	20±3	25±4	87±4	97±2	91±3	93±2	98±3	75±3	21±2	24±2	78±2
15	100±2	93±3	96±4	99±1	87±3	26±4	30±3	90±2	98±4	92±2	94±3	100±1	78±2	25±3	32±3	80±4
30	99±5	92±4	95±3	99±1	90±4	31±3	36±2	96±3	98±2	94±1	96±1	99±2	79±4	31±3	36±3	82±3
60	99±3	96±3	98±4	100±2	94±3	37±2	41±4	97±3	99±3	93±3	96±2	99±2	82±3	36±2	41±2	86±2
90	100±2	97±2	98±3	100±1	97±3	42±4	45±4	96±4	100±2	96±2	97±1	100±1	85±4	40±4	46±3	89±4

[a] Eluting solvents used were hexane and 40% benzene in hexane for aldrin and dieldrin, respectively, and percent recovery of pesticides was determined by GLC.

[b] Silica gel was used as received without any further heat treatment.

[c] Mean deviation of four replicates.

TABLE II

Percent recovery of aldrin and dieldrin from microcolumn packed with 1 gram of silica gel subjected to 2-hour treatment at different temperatures[a]

Days after treatment	Silica gel															
	Grade 950 (60-200 mesh)								Grade 923 (100-200 mesh)							
	Aldrin				Dieldrin				Aldrin				Dieldrin			
	Temperature (°C)															
	Control[b]	130	300	650	Control	130	300	650	Control	130	300	650	Control	130	300	650
1	99±3[c]	91±4	91±3	98±3	79±4	20±2	26±3	84±2	97±3	91±3	91±1	100±2	73±2	16±2	21±1	75±1
5	98±5	92±4	94±2	99±1	83±3	21±3	27±2	89±3	98±4	91±4	93±1	100±2	72±4	18±1	23±2	76±2
10	98±2	93±6	95±5	100±2	88±5	22±3	32±3	90±2	96±3	92±1	93±2	100±1	74±3	20±2	26±1	75±2
15	100±1	93±4	95±2	100±2	89±4	28±2	37±2	93±2	98±4	93±1	93±1	100±3	77±3	23±2	30±2	79±3
30	99±3	93±4	96±1	100±1	92±3	32±3	40±2	95±1	99±2	93±2	94±1	100±1	76±2	26±1	34±2	77±1
60	99±3	95±4	96±2	100±1	96±4	38±4	43±4	94±2	100±2	95±1	95±1	100±1	79±3	32±2	40±3	82±4
90	100±2	98±1	98±2	100±2	96±3	44±4	48±3	95±3	100±3	96±3	97±1	100±2	83±3	38±3	44±2	86±3

[a] Eluting solvents used were hexane and 40% benzene in hexane for aldrin and dieldrin, respectively, and percent recovery of pesticides was determined by GLC.

[b] Silica gel was used as received without any further heat treatment.

[c] Mean deviation of four replicates.