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GAS LIQUID CHROMATOGRAPHIC ANALYSIS OF 2-CHLORO-4-NITROANILINE ON A SUPPORT BASED ON A NON-EXTRACTABLE LAYER OF POLYETHYLENE GLYCOL SUCCINATE ON CHROMOSORB P

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SUMMARY

Using a non-extractable layer of polyethylene glycol succinate (PEGS) on Chromosorb P, additionally coated with a PEGS stationary phase in a short column, a rapid and successful analysis of 2-chloro-4-nitroaniline was achieved. Chromosorb P AW (0.015% Fe) after coating with PEGS has undergone thermal treatment at 300°C in a flow of an inert gas. After this treatment the support was exhaustively extracted and used as a deactivated support with the aid of a non-extractable PEGS layer. The PEGS column quality and resolution ability were tested with various model mixtures: Wright's mixture, low- and high-molecular-weight alcohols, and synthetic fatty acids. Chromatographic parameters such as peak area, resolution criterion and asymmetry coefficient of the analyzed nitroanilines were evaluated statistically and their reproducibility was very good.

INTRODUCTION

In the last decade a number of chromatographic problems have been solved with bonded phases" [1]. The fact that bonded phases provide a surface of reduced activity makes the solution on some basic problems of gas-liquid chromatography (GLC) possible. The problem is due to the undesirable adsorption of the solute in the column (both packed[1–4] and capillary[4–9]).

The successful analysis of polar high-molecular-weight compounds using bonded phases, giving symmetrical peaks, reproducible experimental data and complete elution from the column, has attracted the attention of a number of researchers[10–14]. In connection with this, we have investigated the possibilities of using non-extractable ("bonded") polymer layers for the analysis of nitroanilines. Chloronitroaniline derivatives are used as intermediates for synthetic dye production and pharmaceutical preparations. One possible synthesis in 2-chloro-4-nitroaniline production is chlorination of 4-nitroaniline. Prior to the analysis of nitroanilines, the quality and resolution of the column were tested with various test mixtures of polar and/or high-molecular-weight compounds.

This work shows that by using a support based on a non-extractable layer of polyethylene glycol succinate (PEGS) on Chromosorb P a rapid and successful analy-

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sis of 2-chloro-4-nitroaniline is achieved, which corresponds to the requirements of routine control and analysis in research and factory laboratories.

EXPERIMENTAL

Apparatus

All chromatographic measurements were performed on a Pye Unicam GCV gas chromatograph (Pye Unicam. Cambridge, U.K.), equipped with a flame-ionization detector and an on-column injector. Glass columns (0.5 m × 2 mm I.D.) deactivated with dimethyldichlorosilane (DMCS) were used. The chromatographic conditions are listed in Figs. 1–5.

Thermal treatment of the support was performed using a Carlo Erba GI gas chromatograph (Carlo Erba, Milan, Italy). A glass column (0.5 m × 10 mm I.D.) was fabricated by us[13,14].

A Pye Unicam SP 191 atomic-absorption spectrophotometer was used for the determination of the iron content and a Bruker B-ER 420 electron paramagnetic resonance spectrometer (EPR) (Bruker, Karlsruhe, F.R.G.) for establishing the degree of removal of iron from the support.

All test solutes, solvents and reagents were of analytical or gas chromatographic quality. Chromosorb P was obtained from Johnes-Manville (Denver, CO, U.S.A.), PEGS and PEG 20M from E. Merck (Darmstadt, F.R.G.) and DMCS from Fluka (Buchs, Switzerland).

Preparation of bonded phase packing

Chromosorb P (80 100 mesh) had previously been deactivated by decreasing the iron content to a minimum (below 0.02%). For this purpose washing with 6 *M* hydrochloric acid in a modified Soxhlet[14] apparatus was carried out. Chromosorb P was coated with 5% (w/w) PEGS and had undergone thermal treatment at 300°C in a flow of an inert gas (argon is preferred to nitrogen). The increase in temperature from ambient to 300°C took 5 6 h and the thermal treatment at 300°C was continued for 24 h at a flow-rate of 5 cm^3/min. After this treatment the support was exhaustively extracted with an organic solvent and vacuum dried at 75°C. This support was used as a deactivated support, in this work additionally coated with 3.0% (w/w) of PEGS.

Column test procedure

The quality and resolving ability of the PEGS column were tested with various mode1 mixtures: one similar to that used for testing capillary columns[15] (Fig. la), low- and high-molecular-weight alcohols (Figs. 2 and 3) and synthetic higher fatty acids (Fig. 4).

GLC measurements

A mixture of 2,6-dichloro-4-nitroaniline (A), 2-chloro-4-nitroaniline (B) and 4-nitroaniline (C) had been injected on the PEGS column many times and the column behaviour remained unchanged after 2 years' usage and over 200 injections. The reproducibility of GLC measurements expressed as relative retention times (RRT), asymmetry coefficients ***(k,)*** and resolution criteria (R,,.,) were evaluated statistically from five injections (Table I). For the quantitative analysis of 2-chloro-4-nitroaniline

the relative response factors of the flame-ionization detector were determined and were 1.2, 1 .0, and 0.8 for A. B and C. respectively.

RESULTS AND DISCUSSION

When problems due to the activity of GLC packed columns are considered, the presence of impurities in the solid support. such as iron, aluminium and titanium and their oxides[1–3,10–14], is of great importance as they impart catalytic and adsorption activity to its surface and cause no less deterioration in its homogeneity than do silanol groups. Deterioration of the liquid phase layer is particularly obvious with lower phase loadings on the support; on the other hand, iron and titanium may disturb the bonding of the polymer layer on the support[10,11,16]. This is one of the reasons why the chemical purity of the support has received significant attention with the introduction of bonded phases[10] where the deactivated film of the polymer is below 0.3%.

Of the methods suggested for the reduction of the iron content, such as acid washing[1–3,10,11], treatment with hydrogen chloride at 850–900°C[17], we have employed the first one as it ensures a clean and homogeneous surface and is easily carried out[10–14]. The iron content was reduced to 0.015%, as determined by atomic-absorption spectroscopy. For rapid and easy checking of the degree of removal of iron from the support, the EPR method has been used. as iron has a characteristic spectrum and at low concentrations the signal intensity is proportional to concentration.

Of deactivators of silanol groups on supports, such as linear polyethylenes (PEG 20M), polysiloxanes (SE-30. AN-600). Apiezon L, etc.[2,3] and silanizing agents such as octamethylcyclotetrasiloxane, PEG 20M[1] is used most often. Aue and co-workers proposed a well known method for preparation of a non-extractable polymer layer on a diatomite surface. The suitability of this method of deactivation and the application of PEG 20M have proved adequate many times[1–3,10–14]. Similar deactivating properties were shown by PEGS. which has a higher thermal stability after deactivation (300°C) than PEG 20M (270°C).

Numerous investigations in GLC have been carried out on the possible mechanism of bonding of linear polyethylenes to diatomites and there has been no definite explanation put forth so far. One of the assumptions is that thermal treatment allows a significant part of the long polymer molecule to arrange physically on the support surface, thus resulting in a large number of Van der Waals and/or hydrogen bonds between the support surface and the polymer. However, this has not yet been proved.

As was mentioned above, the analysis of 2-chloro-4-nitroaniline was preceded by testing of the PEGS column. It should be noted that during the last few years the testing of capillary columns has included both qualitative and quantitative experiments. and the method suggested by Grob and Grob[18] has been accepted as a standard in glass capillary GLC practice. For packed columns, however, either no preliminary testing has been carried out or it has been done in different ways. The parameters often used are the theoretical plate number (N) and the capacity ratio (k), which are very important but give no information about the degree of elution of the solute from the column. Bearing in mind that the preliminary testing is of great importance not only for capillary columns but also for packed ones as well, it is necessary to find a suitable method for testing packed columns. One possibility could

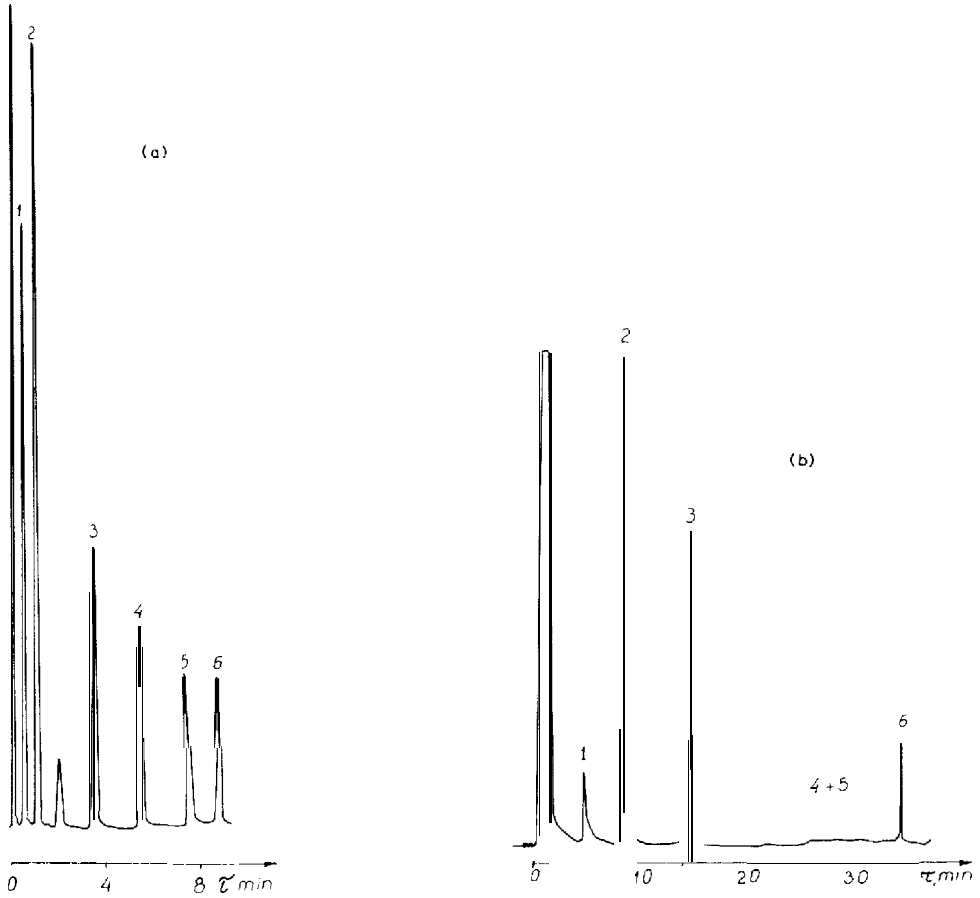

Fig. 1. (a) Test chromatogram of a Wright polarity mixture[15] on a Pyrex glass packed column. Column: 0.5 m × 2 mm I.D., packed with 3.0% PEGS on Chromosorb P AW (0.015% Fe) (80–100 mesh) deactivated with a film of PEGS. Temperatures: column, 70°C isothermal for 1 min then programmed at 10°C/min to 160°C; flame-ionization detector, 260°C; injector, 250°C. Flow-rate, 20 m^3/min; chart speed 0.5 cm/min. Peaks: 1 = 2-heptanone; 2 = 2-octanone; 3 = naphthalene; 4 = *n*-decanol; 5 = n-dodecanol; 6 = n-octadecane. (b) Test chromatogram of a Wright polarity mixture is on a Pyrex glass capillary unleached column. Column: 15 m × 0.3 mm I.D., coated with 0.25 μm SE-52. Temperature: 40°C programmed at 4°C/min to 160°C.

be to use the mixture suggested by Wright *et al.*[15] for testing capillary columns. This mixture is more suitable for packed columns than the Grob and Grob mixture[18] as it contains fewer components.

The PEGS column gives a complete separation of the components present in Wright's mixture (Fig. la); the pair 4-5 (decanol -dodecanol) is retained reversibly whereas on a capillary column it is retained irreversibly (Fig. 1 b) and adequate elution is achieved after long procedures of leaching and silylation[15].

To utilize capillary columns effectively significant investment is necessary, not only for deactivation of the column but also for modification of the detectors, injectors, etc. Chromatographic practice shows that in many instances[2–4,10–14] bonded-

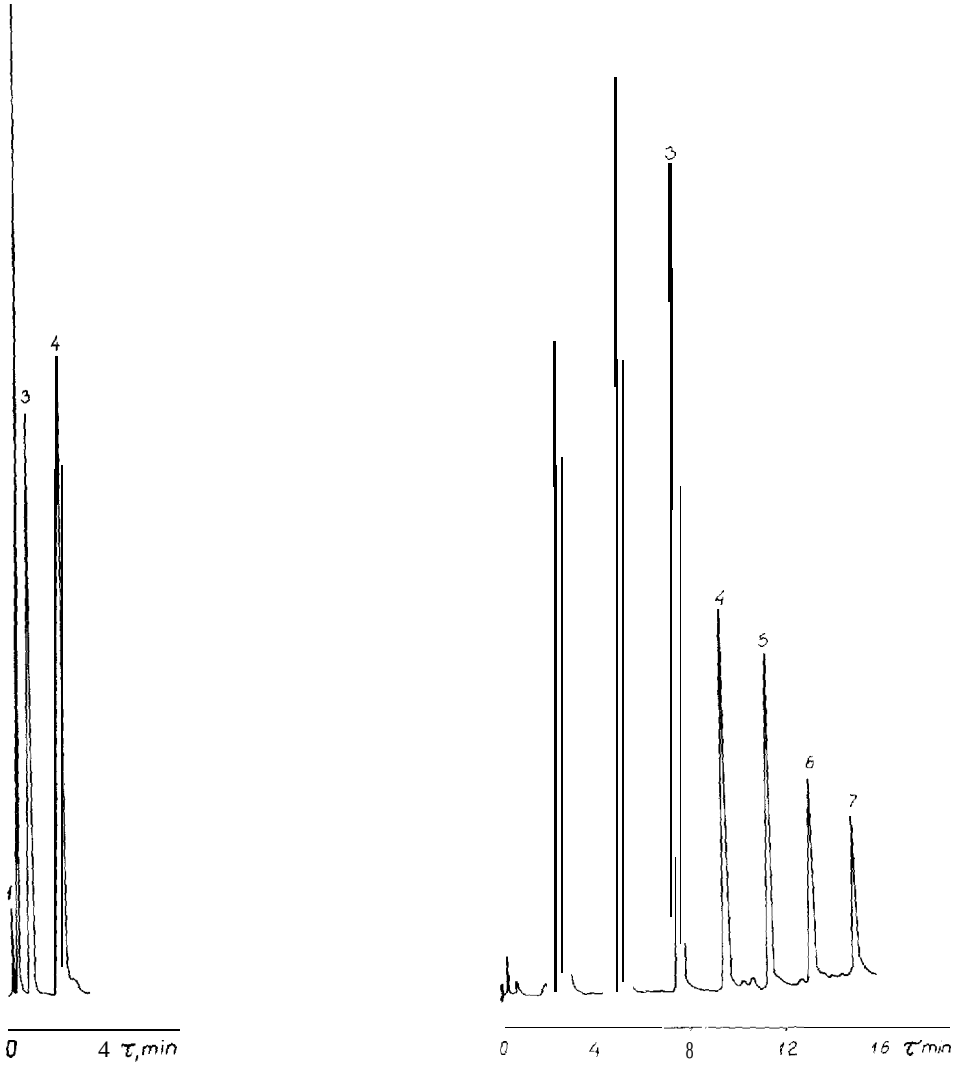

Fig. 2. Chromatogram of a model lower primary alcohol mixture on a PEGS packed column as in Fig. la. Temperatures: column, 50°C isothermal; Aame-ionization detector, 100°C; injector, 80°C. Peaks: 1 = 1-propanol; 2 = I-butanol; 3 = 1-pentanol; 4 = 1-hexanol,

Fig. 3. Chromatogram of a model higher primary mixture (C_6–C_{18}) on a PEGS packed column. Temperatures: column, 50°C isothermal for 1 min, then programmed at 10°C/min to 205°C; flame-ionization detector, 270°C; injector, 260°C. Flow-rate, 20 cm^3/min. Peaks: 1 = I-hexanol; 2 = 1-octanol; 3 = 1-decanol; 4 = 1-dodecanol; 5 = 1-tetradecanol; 6 = l-hexadecanol; 7 = 1-octadecanol.

phase packed columns to a great extent meet the requirements related to good resolution and rapid analysis when separation is not a crucial problem.

The chromatograms in Figs. la and 2-5 show that a proper combination of a deactivated support and a suitable phase and column dimensions give good reso-

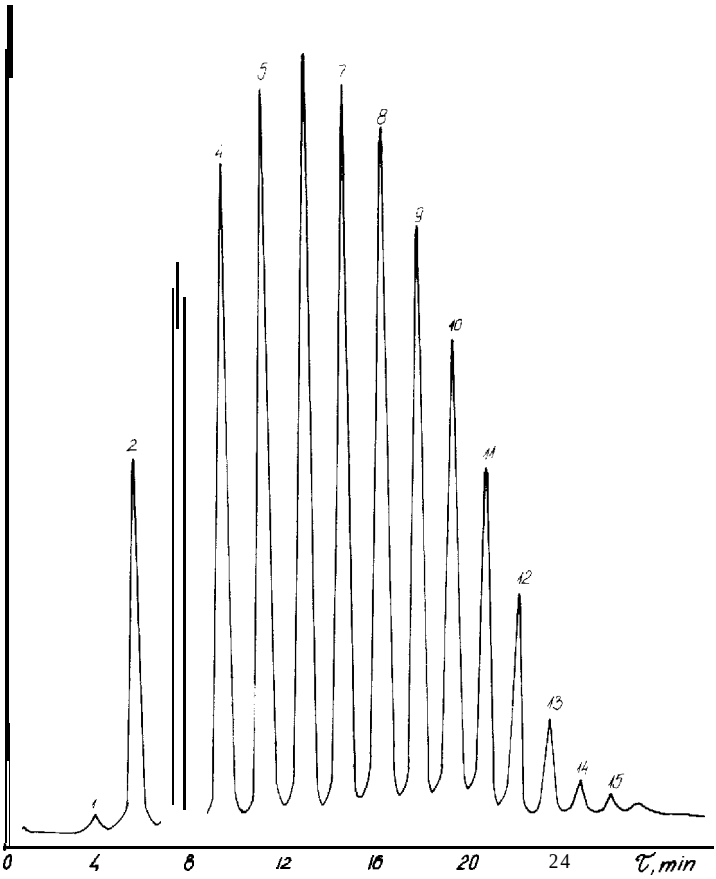

Fig. 4. Chromatogram of a synthetic higher fatty acid methyl ester mixture (C_9-C_{23}) on a PEGS packed column. Temperatures: column, 70°C isothermal for 1 min then programmed at 5.5°C/min to 205°C; flame-ionization detector, 290°C; injector, 260°C. Flow-rate, 35 cm^3/min; chart speed, 0.5 cm/min. Peaks: 1 = pelargonate; 2 = caprate; 3 = undecanoate; 4 = laurate; 5 = tridecanoate; 6 = myristate; 7 = pentadecanoate; 8 = palmitate; 9 = heptadecanoate; 10 = stearate; 11 = nonadecanoate; 12 = eicosanoate; 13 = heneicosanoate; 14 = behanate; 15 = tricosanoate.

lutions of the investigated mixtures, containing polar high-molecular-weight compounds with decreased analysis times. As is well known, a short column not only ensures a short analysis time but also decreases the undesirable adsorption of some compounds resulting from prolonged residence in the column. As a result of the low volatility of bonded stationary phases, analyses with temperature programming can be carried out without a compensation column. Table I shows the evaluation of the constancy of column quality. The peak areas, resolution criteria and asymmetry coefficients of nitroanilines were evaluated statistically; the reproducibility of the chromatographic measurements is good. As already mentioned, the impurities 2,6-dichloro-4-nitroaniline and 4-nitroaniline, are separated completely from the main component, 2-chloro-4-nitroaniline. PEGS showed better selectivity than PEG 20M; the resolution criterion ($R_{t,w}$) of the 2-chloro-4-nitroaniline/4-nitroaniline pair for the

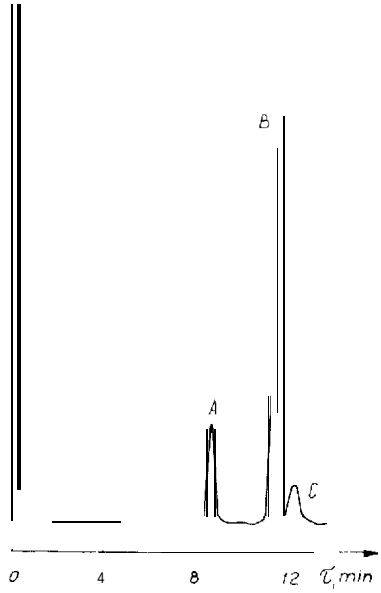

Fig. 5. Chromatogram of 2-chloro-4-nitroaniline (B) in the presence of 2,6-dichloro-4-nitroaniline (A) and 4-nitroaniline (C) impurities. Temperatures: column, 140°C isothermal for 1 min, then programmed at 5°C/min to 205°C; flame-ionization detector, 260°C; injector, 210°C. Column and other conditions as in Fig. la.

PEGS column was 1.5 (Fig. 5) whereas the PEG 20M column with the same dimensions and loading on Chromosorb P did not separate this pair ($R_{t,w}$ = 0.4). Hence the advantage of the proposed column is that it is reasonably selective, inert, and shows low bleeding.

TABLE I

REPRODUCIBILITY OF NITROANILINE RELATIVE RETENTION TIMES (RRT) RESOLUTION CRITERIA ($R_{t,w}$) AND ASYMMETRY COEFFICIENTS (k,) ON A BONDED PEGS COLUMN

A = 2,6-Dichloro-4-nitroaniline; B = 2-Chloro-4-nitroaniline; C = 4-nitroaniline. SD = standard deviation; RSD = relative standard deviation; $\bar{x} \pm \Delta\bar{x}_{95}$ = accuracy of average values at a confidence level of probability a = 0.95.

Parameter	*Nitroaniline*	*Values*					$\bar{x}$	*SD*	*RSD (%)*	$\bar{x} \pm \Delta x_{0.95}$
RRT	A	0.73,	0.72,	0.73,	0.73,	0.72	0.73	0.004	0.55	0.73 ± 0.005
	B	1.0,	1.0,	1.0,	1.0,	1.0	1.0	–	–	–
	C	1.08,	1.08,	1.08,	1.08;	1.07	1.08	0.003	0.27	1.08 ± 0.004
$R_{t,w}$	A	–			–					–
	B	5.7,	5.5,	5.1,	5.2,	5.7	5.4	0.28	4.9	5.4 ± 0.34
	C	1.5,	1.5,	1.4,	1.3,	1.4	1.4	0.07	5.1	1.4 ± 0.09
k_a	A	1.2,	1.2,	1.1,	1.1,	1.2	1.2	0.05	4.7	1.2 ± 0.15
	B	1.1,	1.0,	1.1,	1.1,	1.2	1.1	0.07	6.4	1.1 ± 0.19
	C	1.1,	1.2,	1.2,	1.2,	1.1	1.2	0.05	4.7	1.2 ± 0.15

CONCLUSIONS

The combination of a modified support based on a non-extractable layer of PEGS and column dimensions of 0.5 m × 2 mm I.D. is a good choice for the rapid routine analysis of 2-chloro-4-nitroaniline and of polar and/or high-molecular-weight compounds (alcohols, fatty acids, etc.). The stability of the column ensures a good performance with one column using temperature programming.

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