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THE USE OF PRE-COLUMN TO AVOID THE INTERFERENCE OF POLYAMIDES(NYLONS) IN THE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC ANALYSIS OF SALICYLATES

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A new liquid chromatographic procedure for the determination of salicylic acid and its derivatives in the presence of nylon has been developed. By using pre-column(packing material; silica gel) and main-column(packing material; Hitachi gel 3011), salicylates could be easily determined by means of a UV detector (at 254nm) without any interference of nylon. The average salicylates recovery over a concentration range of 50-800 μg/ml was 99.7±1.3%.

Analysis of salicylates by high-performance liquid chromatography(HPLC)has been reported by several authors.$^{1-4)}$ However, when the sample containing some kind of polymers, which are usually used as the base of cosmetic products and drugs, is directly injected into a column, such determination can not be applied to salicylates, because these polymers which are slightly soluble or insoluble in the solvent as a mobile phase of HPLC adhere onto the column packing material.

Therefore, a modification of HPLC was studied in order to analyze salicylates without interference of polymer. It was tried to remove polymer with a short pre-column and to separate salicylates each other with a long main-column. In this study, a polyamide(nylon) was employed as an example of the polymers. This nylon was a stoichiometric copolymer(Ultramide 1C, BASF Co., Ltd.) derived from caprolactam, hexamethylenediamine adipate and 4,4-diaminodicyclohexylmethane adipate.

At first, it was investigated to find the suitable packing material for pre-column. In this case, the suitability of pre-column packing materials was checked by occurrence of turbidity in the solution which was added acetone, after passed through the pre-column. In addition, FT-IR (JEOL, Model JIR-40) was used to observe whether nylon was held onto the pre-column packing material surface or not. From the results of this experiment, it was found that silica gel(particle size: <74μm) and anhydrous sodium sulfate(particle size: <74μm) were satisfactory packing materials to hold nylon. Other substances(talc, starch, celite, alumina, charcoal, zinc powder, calcium oxide, cellulose powder, dextran) examined were unsuitable for holding nylon.

Secondly, it was investigated to separate and determine salicylates containing nylon. Table 1 shows the results of our experiments to separate salicylic acid and its derivatives in nylon solution. The operating conditions for analysis are as follows: The liquid chromatograph (Perkin Elmer, Model 1220) with a UV detector (254 nm) was used with 99.5 vol% ethyl alcohol solution as a mobile phase. In a 30 mm x 4 mm i.d. pre-column, silica gel (Wako Pure Chemical Industries, Ltd. about 70 μm) was packed, while in a 1,000 mm x 4 mm i.d. main-column, Hitachi gel 3011(copolymer of styrene and divinylbenzene) was packed. The solvent flow rate was 1.1 ml/min (at an inlet pressure of about 2300 psi) at a room temperature. One to ten μℓ of samples(0.02 mol/ℓ) was injected.

The calibration curves between peak height and amount of sample for glycol salicylate and phenyl salicylate were linear in the range of 50 to 800 μg/ml, and methyl salicylate was used as an internal standard(Recovery: 99.7±1.3%).

From these results, it was found that the analytical method using pre-column was useful for simple and accurate separation and determination of salicylates without any interference of polymer such as nylon.

Table 1 Experimental results

No.	Sample*	Tr.** (min)	Peak Height Ratio
1	Methyl Salicylate	31.0	1.00
2	iso-Propyl Salicylate	28.4	1.14
3	Salicylic Acid	20.6	0.26
4	iso-Butyl Salicylate	32.7	0.93
5	Ethyl Salicylate	30.0	1.09
6	O-Methoxybenzoic Acid	20.1	1.57
7	n-Propyl Salicylate	29.8	1.12
8	iso-Amyl Salicylate	34.4	0.85
9	n-Hexyl Salicylate	47.6	0.63
10	cis-3 Hexenyl Slicylate	43.0	0.89
11	O-Ethoxybenzoic Acid	19.3	2.26
12	Glycol Salicylate	17.7	3.35
13	Salicyl Anilide	23.1	38.18
14	Phenyl Salicylate	59.7	2.25
15	Acetyl Salicylic Acid	18.3	0.37
16	Salicylamide	16.3	4.98
17	n-Butyl Salicylate	36.3	0.86
18	Sodium Salicylate	19.0	0.52
19	Salicyl Aldehyde	28.1	22.87
20	Benzyl Salicylate	63.8	0.57
21	P-Hydroxy Benzoic Acid	16.8	27.69
22	Sulfo Salicylic Acid	22.3	0.39
23	O-Anisaldehyde	33.2	17.65
24	Salicylaldoxime	21.9	34.78

* : Each sample contained the salicylate (0.02 M) in nylon(5%) solution of ethyl alcohol(80 vol%).

** : retention time

References

1) G. W. Peng, M. A. F. Gadalla, V. Smith, A. Peng and W. L. Chiou, J. Pharm. Sci., 67, 710 (1978).
2) So. Jansson and I. Andersson, Acta. Pharm. Suec., 14, 161 (1977).
3) V. D. Gupta, J. Pharm. Sci., 66, 110 (1977).
4) G. Chevalier, P. Rohrbach, C. Bollet and M. Caude, J. Chromatogr., 138, 193 (1977).

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