XXXV	Dihydrothebainoneφ	1.52	opening the ether ring, $\Delta_{5,6}$, $\Delta_{8,14}$, C_4-OH, C_6-OCH_3
XXXVI	14-Acetoxydihydrocodeinone	1.52	C_6=O, $C_{14}\beta$-OAc
XXXVII	Dihydrothebainone	1.61	opening the ether ring, C_4-OH, C_6=O
XXXVIII	N-Propalgyl-14-hydroxydihydro-norcodeinone	1.69	C_6=O, $C_{14}\beta$-OH, N-$CH_2C\equiv CH$
XXXIX	Sinomenine methyl ether	1.87	antipode, opening the ether ring, $\Delta_{7,8}$, C_4-OCH_3 C_6=O, C_7-OCH_3
XL	14-Hydroxydihydronorcodeinone	1.91	C_6=O, $C_{14}\beta$-OH, N-H
XLI	Dihydrosinomenine	2.00	antipode, opening the ether ring, C_4-OH, C_6=O C_7-OCH_3
XLII	14-Hydroxydihydrothebainone	2.45	opening the ether ring, C_4-OH, C_6=O, C_{14}-β-OH
XLIII	Sinomenine	2.83	antipode, opening the ether ring, C_4-OH, C_6=O C_7-OCH_3, $\Delta_{7,8}$

Apparatus : Barber Colman Model 10, Argon ionization detector, 6 ft×8 mm., 1% SE-30 on gas-chrom P (100~140 mesh)
Condition : Column temp. 185°, Cell temp. 160°, Flash heater temp. 280°, Argon pressure 2 kg./cm^2
Sample : 0.5~1% Me_2CO solution were used except in the case of morphine (XXII) in which 0.5% MeOH solution was used
Standard : Codeine=4.71 min.=1 R.R.T.

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Teflon Coated Support for Gas Chromatography at a Lower Temperature

The gas chromatographic analysis has no doubt been a very effective tool for chemis ts, but there is a narrow limitation of tailings which occur inevitably when the analysis is done at a lower temperature, with strongly polar substances and/or on the packings containing minor amount of stationary liquid (e.g. 0.1~10%).

Many attempts which have been done to reduce such tailings, can be classified as follows; a) use of new support. e.g. salts,[1] glass beads,[2] sea sand,[3] quartz. powder,[4] metal helices,[5] Tide[6] or Teflon powder,[7] b) improvement of firebrick or Celite, e.g.

1) F.R. Cropper, A. Heywood : Nature, **174**, 1063 (1954).
2) C. Hishta, J.P. Messerly, R.F. Reschke, D.H. Fredericks, W.D. Cooke : Anal. Chem., **32**, 880 (1960).
3) Y.R. Naves : J. Soc. Cosmetic Chemists, **9**, 101 (1958).
4) T. Matsuura, T. Aratani, H. Komae, S. Hayashi : J. Chem. Soc. Japan, Industrial Chemistry Section, **64**, 799 (1961).
5) I. Sörensen, P. Söltoft : Acta Chem. Scand., **10**, 1673 (1956).
6) A.W. Decora, G.U. Dinneen : Anal. Chem., **32**, 164 (1960).
7) M. Sakata, S. Sato, S. Yasui : Abstracts of Papers, 15th Meeting, Chem. Soc. Japan, p. 194 (1962).

through silicon treating,[8,9] polyethylene glycol coating,[10] polycarbonate coating,[11] silver plating[12] or heating at 1000°C for several hours.[13] The fatal defection of the former is the deficiency of the resolving power owing to the limited surface area. Only Tide, having a sufficient resolving power, has been used widely in the analysis of pyridines. On the other hand, the latter, improved supports, show a better resolution, but they have still many defects; the troublesome procedure of improvement : unfavourable selectivity and unstability at a higher temperature of the tailing reducers.

In the present study, the authors found that Teflon coated firebrick or Celite was an improved support which could be used in wide range without tailing. The coating of Polyflon*1 to the refined firebrick or Celite was done in the ordinary manner of coating, using a water dispersion*2 of Polyflon.

Water was evaporated carefully in a reduced pressure below 80°C so that Polyflon dispersion might not be coagulated. The liquid phase was, then, placed on the Polyflon coated support in the usual manner. The comparison of Teflon coated and uncoated supports is shown at Table I.

TABLE I.

Exp. No.	1	2	3	4	5	6
Packing[a]	(A)	(A)	(B)	(C)	(D)	(E)
Temperature (°C)	44	44	44	45	46	45.5
Flow rate (ml./min.)	33	33	30	33	33	30
Sample size[b] (μl.)	1	20	1	1	0.3	0.2
Reaction time (min.)	2.6	2.4	2.7	4.4	2.4	2.7
Number of theoretical plate	100	330	90	420	320	330

Sample; Methanol   Carrier gas; Nitrogen
Column; 4 mm. (inner diameter) × 1 m. Stainless steel   Detector; Katharometer

a) Packing (A) 100:5 (w/w) Dibutyl phthalate on firebrick*3
(B) 100:5 (w/w) Dibutyl phthalate on acid washed firebrick
(C) 100:20 (w/w) Dibutyl phthalate on firebrick
(D) 100:5 (w/w) Dibutyl phthalate on 100:12 (w/w) Polyflon coated firebrick
(E) 100:5 (w/w) Dibutyl phthalate on 100:24 (w/w) Polyflon coated firebrick

b) The sample size was determined so as to give the same peak height with the exception of Expelimental 2.

As is seen in Table I, Teflon treated support have a desirable character for a quick, small sample size, high sensitivity, low temperature and/or strongly polar substances analysis. The rather smaller number of theoretical plate and asymmetrical peak of Expelimental 1 shows that the adsorption of methanol on the column packings cannot, be ignored even at 44°C and 100:5 of stationary phase.

The very same column, however, gives the same number of theoretical plate as that of Teflon coated one, when larger amounts of the sample are injected. (Exp. 2). It will be likely, therefore, that the adsorption on the Teflon coated support is very small. This becomes more obvious with a longer column and at a lower tem-

8) J. Bohemen, S.H. Langer, R.H. Perett, J.H. Purnell : J. Chem. Soc. **1960**, 2444.
9) Akune, Matsuda, Akiyoshi : Abstracts of Papers, 14th Meeting, Chem. Soc. Japan, p. 5 (1931).
10) T. Johns : "Gas Chromatography 1958," p. 31 (1958), edited by V.J. Coates, *et al.* Academic Press Inc., New York.
11) T. Matsuura, T. Aratani, H. Komae : Abstracts of Papers, 15th Meeting, Chem. Soc. Japan, p. 198 (1962).
12) E.C. Ormerod, R.P.W. Scott : J. Chromatog., **2**, 65 (1959).
13) U. Takayama : J. Chem. Soc. Japan, Industrial Chemistry Section, **64**, 803 (1961).

*1 Tetrafluoroethylene polymer (=Teflon) produced by Osaka Kinzoku Kogyo Co., Ltd.
*2 Polyflon Dispersion contains a nonionic surface active reagent, which makes it easier to coat Polyflon to SiOH groups of firebrick, and reacts as a tailing reducer, too.
*3 Isolite N-4 (30～50 mesh) was used.

perature, where the adsorption will be more fatal (Table II).

Table II.

Exp. No.	7	8	9	10
Packing	(A)	(D)	(D)	(D)
Column length (m.)	2	2	2	3
Temperature (°C)	46	46	3	32
Flow rate (ml./min.)	30	33	120	21
Sample size (μl.)	1	0.5	2	1
Reaction time (min.)	6.0	5.0	10.2	21.9
Number of theoretical plate	47	670	832	1500
Tailing	+++	±	±	±

Sample; Methanol   Carrier gas; Nitrogen
Column; 4 mm. (inner diameter), Stainless steel   Detector; Katharometer

Celite can also be improved with Teflon coating. The results of the experiments are summarized in Table III and Fig. 1.

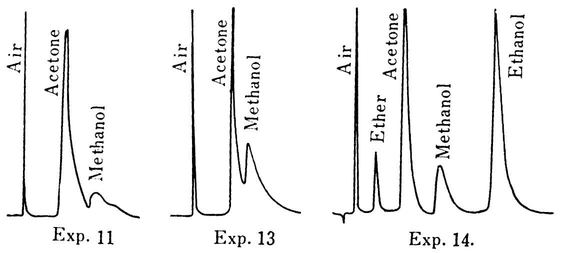

Fig. 1.

Table III.

Exp. No.	11		12		13		14	
Packing[a]	(F)		(G)		(H)		(I)	
Temperature (°C)	25		22		22		22	
Flow rate (ml./min.)	70		58		60		62	
Samle size[b] (ml.)	0.5		0.5		0.5		0.5	
Sample	A	M	A	M	A	M	A	M
Reaction time (min.)	1.3	2.8	1.6	2.0	1.7	2.3	2.5	3.9
Number of theoretical plate	78	16	335	101	340	144	380	277
Tailing	+++	+++	−	+	−	+	−	±

Sample; Mixture of acetone (A) and methanol (M)   Carrier gas; Helium
Column; 4 mm. (inner diamerter) × 2 m. Stainless steel   Detector; Katharometer

a) Packing (F) 100:2(w/w) Dinonyl phthalate on Celite 545
(G) 100:2(w/w) Dinonyl phthalate on 100:10(w/w) Polyflon coated Celite 545
(H) 100:2(w/w) Dinonyl phthalate on 100:20(w/w) Polyflon coated Celite 545
(I) 100:2(w/w) Dinonyl phthalate on 100:30(w/w) Polyflon coated Celite 545

b) A described amounts of the air was charged that was saturated with acetone and methanol at room temperature. (20°C)

As the volume weight of the Teflon coated Celite is different from that of the original uncoated Celite, the comparison of these support is very difficult. Although the coating might as well be done in proportion to the surface area of support, the simple coating proporsal to the weight of support was adapted. The qualitative results of these experiments might not change, however, on the ground that the number of theoretical plate improvement of methanol is far greater than that of acetone.

The various kinds of hardly volatile compounds can be separated at a lower temperature without tailings when these improved support is used.

For example, *o*-phenylphenol (b.p. 275°C), diphenyl ether (b.p. 259°C) and phenol was separated successfully at 156°C. This was accomplished on the 1 m. column of 100:20

Polyflon coated support with 100:10 SanVac grease (paraffin wax) as a stationary phase. Their retention volumes were 2340, 1153 and 132 ml. respectively (flow rate 156 ml./min.).

The authors have had successful results in the analysis of pyridines, higher fatty acids themselves, terpenes and others using Teflon coated column support which will later be published elsewhere.

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