grams obtained under low pressure mode show sharper peaks than those obtained under normal mode. In the case of formic and propionic acids, the impurities which appeared as shoulders during the normal mode, gave sharp and well resolved peaks during the low pressure mode.

The method appears to hold out several advantages over the normal gas chromatographic analysis. Some of these would be the study of high boiling or low volatile compounds, and analysis of heat-labile compounds in addition to the faster elution and better resolution. A detailed work covering the study of these factors and others has been undertaken, and the results will be reported in subsequent communications.

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Received August 26th, 1968

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CHROM. 3904

A new sampler for gas chromatographic analysis of liquids and solutions

According to LEIPNITZ AND STRUPPE[1], one of the most important prerequisites for exact analysis is that the amount of injected material and the method of introduction be as precisely reproducible as possible. The samplers presently available fulfil this condition only partially and also present cleaning difficulties, especially when viscous substances are used. Nor do they have a constant injection pressure, except when used with the "Reprojector"*. This reprojector, however, is even more difficult to clean than the other samplers. Thus we have tried to develop an improved sampler which eliminates these deficiencies and at the same time permits a high degree of reproducibility.

Fig. 1 shows the newly developed sampler** which consists of two parts: a syringe, which does not come into contact with the test mixture, and a calibrated component, namely an interchangeable cannula made of stainless steel. The syringe is a standard 2 ml syringe modified by the addition of a pressure relief valve. The method of operation is illustrated in Fig. 2. The 2 mm^3 cannula containing the test sample (5) is attached to the cone of the air-filled syringe. Automatically the rear, wider end of the cannula (11) depresses the cylinder (8)—made airtight by a gasket (12)—of the pressure relief valve, thus effectively sealing the cannula. Next, the needle is inserted into the injector of the gas chromatograph and the plunger (2)

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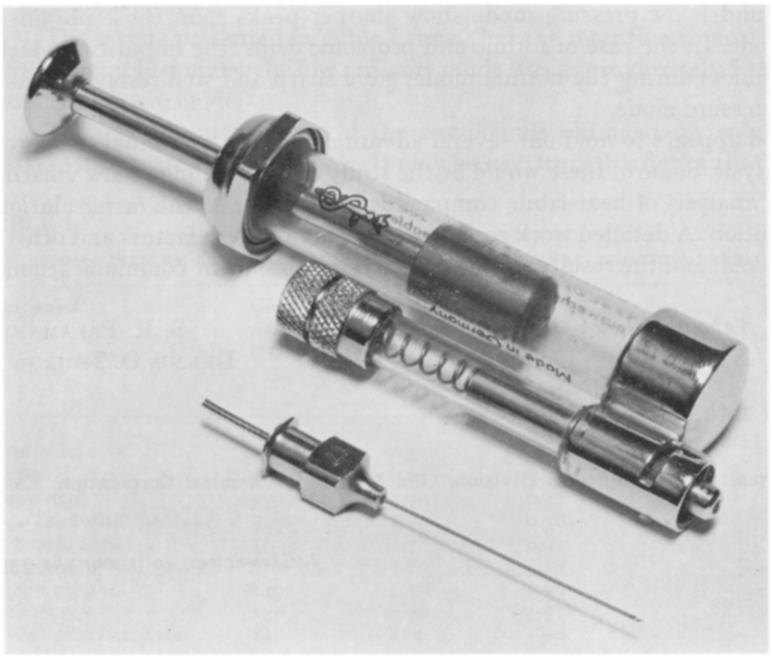

Fig. 1. Sampling device.

activated. The spring (7) is depressed only when the pressure exceeds that of the carrier gas, thus introducing the sample into the injector. The injection pressure remains constant throughout the operation.

Considerable care must be exercised in filling the cannula during quantitative experiments. The following procedure is recommended: place a transparent tube of plastic or silicone rubber over the rear end of the cannula and, through it, draw up the test mixture to a level of 1 cm. Attach a piece of tubing approximately 1 cm long to the front (pointed) end of the cannula and blow the sample through the cannula from back to front so that the surplus mixture is equally distributed between the tubes at the two ends of the cannula. Remove the tubing from the wider end, wipe the upper section of the cannula clean with a small piece of filter paper and then press the paper over the opening to draw off part of the test mixture from the front end of the cannula. Attach the cannula to the air-filled syringe. The tubing at the front end is removed immediately before injection into the gas chromatograph. The entire procedure outlined above takes approximately 30 sec. The cannulas are cleaned in the same way as pipettes (by blowing through water, solvent or air).

The degree of reproducibility was tested using cannulas with capacities of 2 μl and 0.5 μl. In the first series of experiments (2 μl) twelve injections were carried out with four different alcoholic solutions (Merck). The results are shown in Table I.

Table II shows the results obtained in the test series using the 0.5 μl cannula. For experiment (a) we employed a 1‰ alcoholic solution with a recorder attenuation of 32 $\times$ which produced a relatively low peak, while for experiment (b) we used

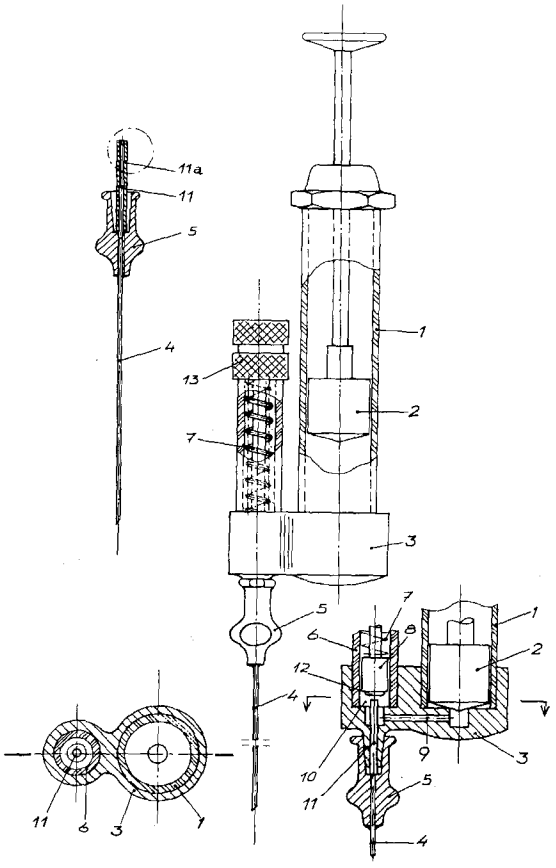

Fig. 2. Plan of sampling device.

TABLE I

DEGREE OF REPRODUCIBILITY USING CANNULAS WITH CAPACITIES OF 2 AND 0.5 μl AND DIFFERENT ALCOHOLIC SOLUTIONS

	(*a*) 0.8 ‰		(*b*) 1.6 ‰		(*c*) 2.8 ‰		(*d*) 3.0 ‰	
Peaks	63.2	64.2	65.0	64.5	113.1	113.9	120.5	121.0
	62.4	62.9	65.1	64.8	114.4	113.9	120.8	118.7
	64.0	63.5	64.6	64.6	113.2	114.8	120.1	119.9
	63.0	63.8	64.7	65.8	113.9	112.8	119.2	120.8
	64.2	63.2	63.5	63.8	113.2	112.8	120.0	120.6
	63.4	64.1	65.2	64.9	114.0	113.8	121.2	120.2
Mean values	63.5		64.7		113.6		120.2	
Deviation (%)	0.91		0.94		0.56		0.60	

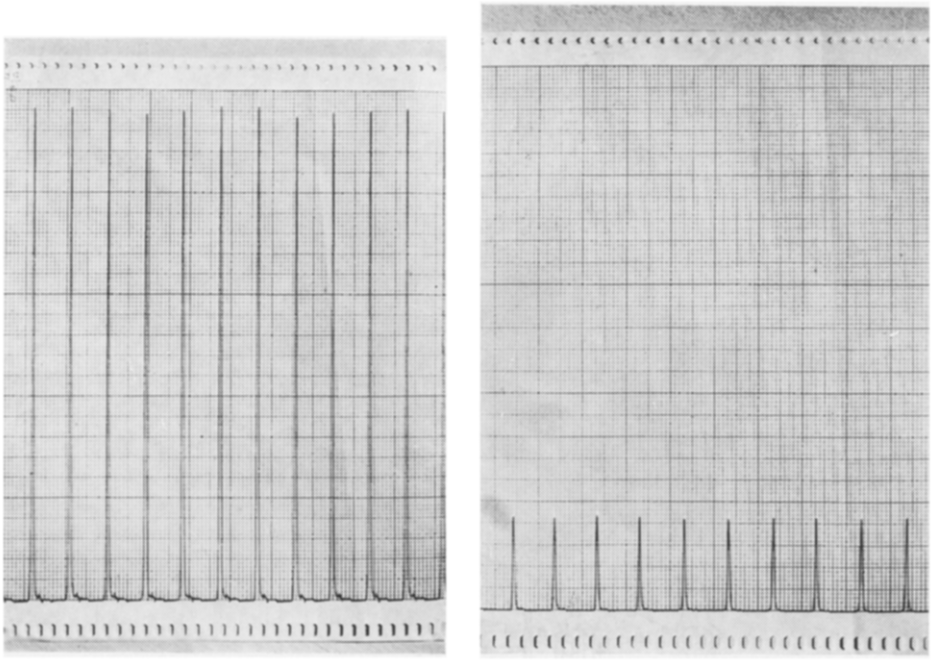

Fig. 3. (a) Results using 2 μl of a 3.0‰ solution of ethyl alcohol in water (Table Id); (b) results using 0.5 μl of a 1.0‰ solution of ethyl alcohol in water (Table IIa).

TABLE II

DEGREE OF REPRODUCIBILITY USING A CANNULA WITH A CAPACITY OF 0.5 μl AND DIFFERENT SOLUTIONS

	(*a*) 1.0 ‰ *alcoholic solution*[a]		(*b*) *Benzol*[b]		
Peaks	21.3	20.9	75.9	76.3	74.3
	21.2	21.2	74.7	75.3	74.7
	21.7	21.2	75.2	75.0	75.5
	21.5	21.4	76.0	75.2	74.6
	20.9		76.5	74.9	75.3
	20.9		76.0	75.6	74.9
Mean values		21.3		75.3	
Deviation (%)		1.17		0.82	

[a] Recorder attenuation 32 ×
[b] Recorder attenuation 3200 ×.

benzol with a recorder attenuation of 3200 ×. The peaks were measured in all experiments.

The following conditions prevailed: Varian aerograph 1525; detector, F.I.D. 150°; injector, 125°; columns, Hellcomid 100/120 mesh, Chromosorb white/hexamethyldisilicane 78°; carrier gas, N_2, 30 cc/min.

The mean error was calculated according to the usual formula

$$\xi = \sqrt{\frac{\Sigma(Mv - M)^2}{n - 1}}$$

with M representing the measured value, Mv the mean value ($Mv = \Sigma M/n$, and n the number of experiments performed. The tables demonstrate that the degree of reproducibility achieved was sufficiently high to meet the standards demanded in exacting analytical work despite the fact that neither an internal standard nor an integrator was used.

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1 LEIPNITZ AND STRUPPE, *Handbuch der Gaschromatographie*, Verlag-Chemie, Weinheim, 1967.

First received November 7th, 1968; revised manuscript received December 9th, 1968

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