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DIRECT SAMPLING OF SLURRIES FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF VOLATILE COMPOUNDS

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SUMMARY

An apparatus has been constructed which can be used for introducing slurries directly into a gas chromatograph in order to determine their volatile constituents. The dry matter of the sample is removed from the apparatus after each determination. The sample-introducing system developed can be used up to a temperature of 230° and a pressure of 6 kg/cm², without causing any change in the chromatographic parameters. The system has favourable operation properties, such as easy maintenance and control. The apparatus has been successfully used for more than a year for the serial determination of ethanol in blood samples by gas chromatography.

INTRODUCTION

Our task has been to construct a gas chromatographic (GC) analytical system and apparatus for the determination of methanol, ethanol, and acetone in 150–200 blood samples with an accuracy of ±5% in an 8-h working-day. The apparatus, designed by Machata[1–3] and produced by Perkin-Elmer (Überlingen, G.F.R.), can make two parallel analyses on 50 blood samples within the working-period given[4,5].

Some of the problems to be solved in developing the GC procedure required were connected with the introduction of a sample (slurry) containing great amounts of non-volatile components into the gas chromatograph. As the determination of volatile components in slurries by GC has become a common problem in chemical analysis, we wish to publish our experiences in the present paper.

A special difficulty in the GC analysis of slurries is ensuring that only the vapours of the components to be determined enter the column, as any solid material blocks up the gas pathways or the whole column, thus falsifying the results of analysis or even rendering the analysis impossible.

The introduction of sample into the column is also critical in most cases because of the necessity of optimizing the time of analysis and the special requirements of quantitative analysis, as shown by Peterson and other workers[6,7] on the basis of experimental and theoretical studies. Any deviation in the sample introduction from instantaneousness and square-wave impulse results in a considerable distortion of the peaks and consequent interference.

In the case of capillary columns the difficulties due to splitting are well known[8,9].

With slurries, however, owing to problems connected with sample introduction, after injection a further splitting is necessary, even with packed columns, in order to reduce peak distortion caused by overloading.

Several methods have been developed for eliminating the interfering effects mentioned, such as using filters or reactors before the column to prevent contaminants from entering the column, or the use of various preparation techniques applied to the sample prior to GC analysis (extraction, distillation, analysis of the vapour phase, re-injection, etc.)[10–16].

SAMPLE INTRODUCTION

A method and device have been developed by which not the sample is transformed in a way to enable GC analysis to be carried out in the usual way, but the apparatus is modified so that slurries can be introduced directly for the analysis of volatile components (Fig. 1).

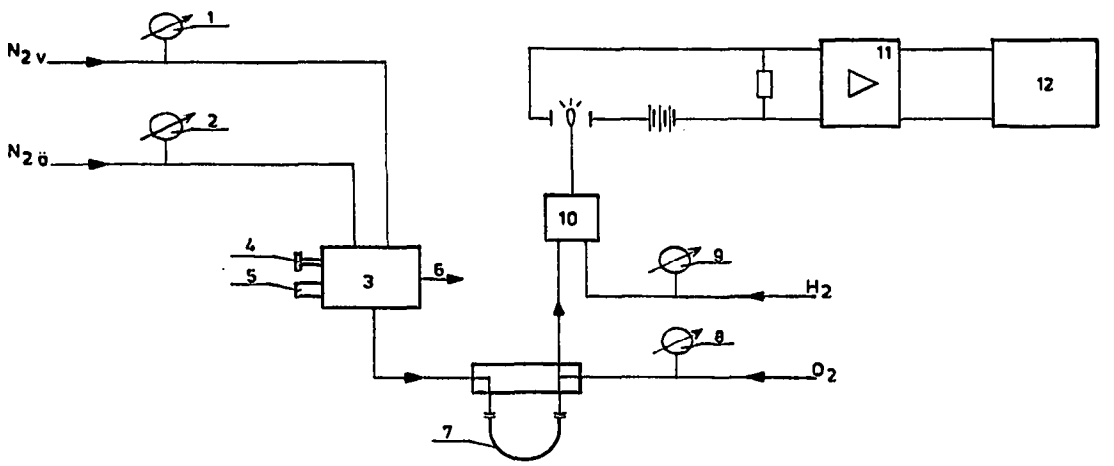

Fig. 1. Schematic of apparatus. 1 = Flow control of nitrogen carrier gas; 2 = flow control of nitrogen flushing gas; 3 = gas-flow switching tap; 4 = "injection" sample-introducing inlet; 5 = "boat" sample-introducing inlet; 6 = "flushing" outlet; 7 = column; 8 = oxygen flow control; 9 = hydrogen flow control; 10 = detector; 11 = amplifier; 12 = recorder.

The components of the sample which can be volatilized are evaporated in a boat-shaped vessel (5) in the evaporator at a temperature higher than the boiling point, and a calibrated, pre-determined amount of the vapour mixture is flushed into the column by means of a gas-flow switching tap (3) operated according to a variable, automatic programme. The carrier gas, according to the position of the tap, flows on to the column (7) either in the path involving the usual sample injection system (4) or through the calibrated sampling space with static splitting, which is connected to the evaporator incorporating the boat (5). The dry matter in the sample is left in the boat (Fig. 2) and can be removed after each run.

The evaporator and the tap can be cleaned after each analysis by flushing with nitrogen gas from a system incorporated especially for this purpose.

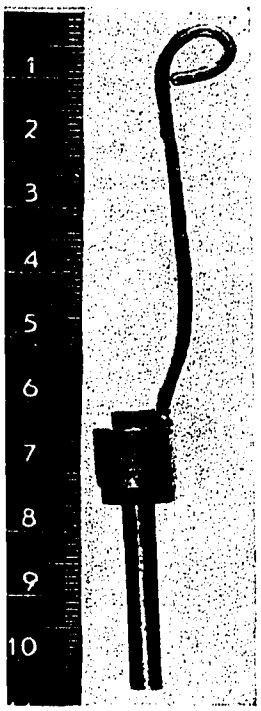

Fig. 2. General view of the sample-introducing boat.

The system described for sample introduction serves several functions (Fig. 3). It evaporates the volatilizable components of the sample containing some liquid (V_f) and the non-volatile residue (M) practically completely to produce a vapour (V_{g1}), and introduces into the column a pre-determined amount (V_{g2}) according to the splitting

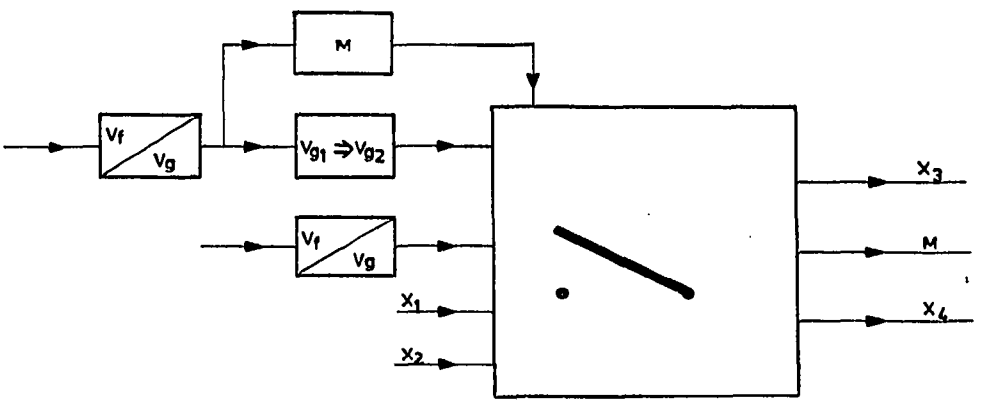

Fig. 3. Flow diagram of the sample-introducing system. V_f = Liquid fraction of sample; V_g = sample component transferred into the vapour phase; M = non-volatile fraction; V_{g1} = fraction of sample transferred into the vapour phase; V_{g2} = amount of sample introduced into the column; X_3 = analytical column; X_4 = residual sample amount.

ratio (X_3) and removes the remaining portion of the volatile matter (X_4) and the non-volatile components (M) from the sampling space, thus making ready the apparatus for a new run. In addition, the system can also be used with the usual sample injection technique (V_f/V_g). The housing (3) of the sample-introducing system (Fig. 4) is made of stainless steel and incorporates channels for sample introduction (5) and flushing.

All the channels fall on the same horizontal, where a plane piston-valve (1) serves for switching the gas paths. The piston-valve, which is flexibly fitted to the metal housing of the system, is made of PTFE. Thus the evaporator, sample-introducing system and gas-stream switch system consist of two functional parts. The pis-

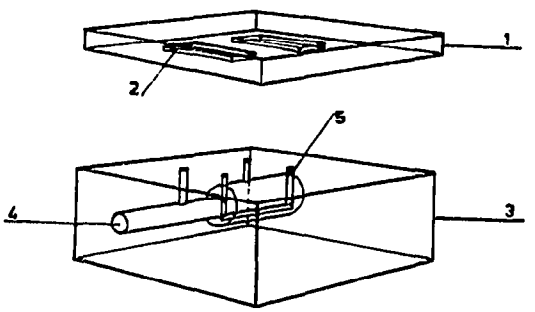

Fig. 4. Sketch of the sample-introducing system. 1 = Plane PTFE piston valve; 2 = grooves of the piston valve; 3 = stainless-steel housing; 4 = inlet for sample introduction by boat; 5 = channels.

ton-valve serving for gas stream switching is operated automatically by a system of Mecman pneumatic elements controlled by a programming system constructed in our laboratories. The system is constructed so that the programme can be changed at will, and, if necessary, can be operated manually. The space serving for introducing samples into the column is a cylindrical boring of 2-mm diameter, with a volume of 380 μl. The volume of the space which is part of the static splitter and serves for flushing can be adjusted according to the splitting ratio.

The boat used for sample injection is made of brass sealed by means of silicone rubber. Its gas-tight fitting to the evaporator is ensured by a simply operated mechanical closing system (Fig. 5). The sample-introducing system is constructed so that it does not place special demands on the gas chromatograph to which it is fitted. In the gas chromatograph constructed in our laboratories the sample-introducing system, column and detector form one unit and can be removed together after loosening the screws and disconnecting the gas tubes.

RESULTS

The sample-introducing system described has been tested by measuring the parameters which affect its applicability in GC, and by applying it to a practical analytical task.

The measurements were made by using a self-made gas chromatograph, a flame ionization detector, a Pye wide-range amplifier (Pye-Unicam, Cambridge, Great Britain), a Honeywell recorder with 2.5-mV total deflection (time constant 0.1 sec)

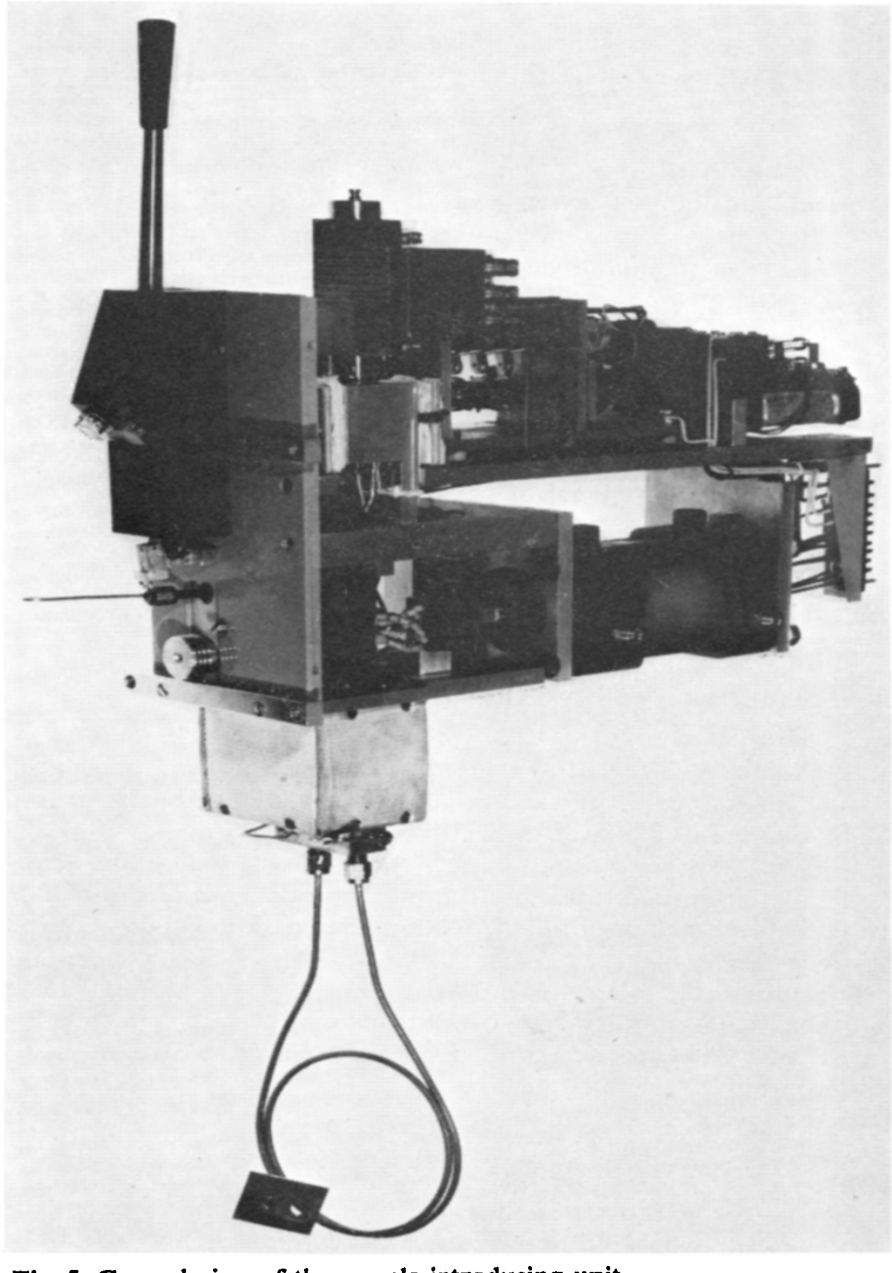

Fig. 5. General view of the sample-introducing unit.

(Honeywell, Fort Washington, Pa., U.S.A.), and a Type HP 3370 B electronic digital integrator or an Autolab Type IV integrator (Autolab, Mountain View, Calif., U.S.A.). Any changes from this apparatus are indicated for the measurements concerned.

Measurements of basic parameters

Baseline stability. At the GC sensitivities applied no appreciable change could be observed in the baseline on changing the position of the gas-flow switching tap or on sample introduction.

Splitting ratio. In consequence of the static nature of the splitter the splitting ratio for the components of the sample does not change with their molecular weights. However, the sample-introducing system is sensitive to the amount of sample. The construction of the system ensures that the splitting ratio does not change even if the amount of sample weighed into the boat changes to an extent exceeding the usual error by one order of magnitude (see Fig. 6).

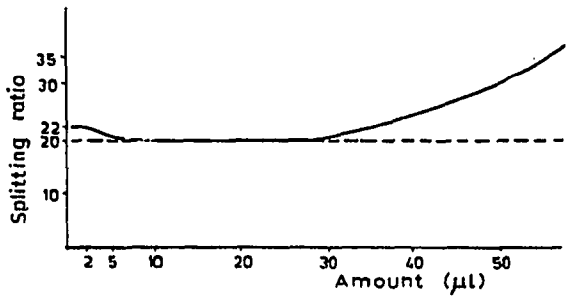

Fig. 6. Dependence of splitting ratio on amount of sample.

The typical curve shown in Fig. 6 shows clearly that, in the case of sample volumes optimized at 20 μl, introduced using the boat, only the deviations exceeding +8 or −12 μl lead to any change in the splitting ratio.

Leak rate. This was studied for sample vapour pressures equal to the overpressure of the carrier gas, for an interval of 0 to 10 min, using delayed flushing. The sample loss was 0.2 μl/min or less, as determined by the quantitative evaluation of the chromatograms obtained.

By increasing the amount of material introduced into the sampling-space, using otherwise unchanged GC parameters, the correlation between the vapour pressure of the sample and the leak-rate was determined on the basis of the quantitative evaluation of the chromatograms.

A typical curve is shown in Fig. 7. Below a pressure of 13 kg/cm^2 no increase in leak-rate could be observed.

Contamination in the case of direct introduction of slurries. Contamination of the evaporator by the dry matter of the sample was prevented by using the boat for sample introduction, so that the non-volatile residue was held back and could be removed when necessary. For example, when serial alcohol determinations were made from blood, the apparatus had to be cleaned only after a year (after about 20,000 analyses).

Effect of sample introduction on the shape of GC peaks. If the partial pressure of the sample in the vapour phase is commensurable with that of the carrier gas, then the instantaneousness is determined by the volume of the sampling space and time of flushing. The influence of sample injection on the symmetry of the curve was studied

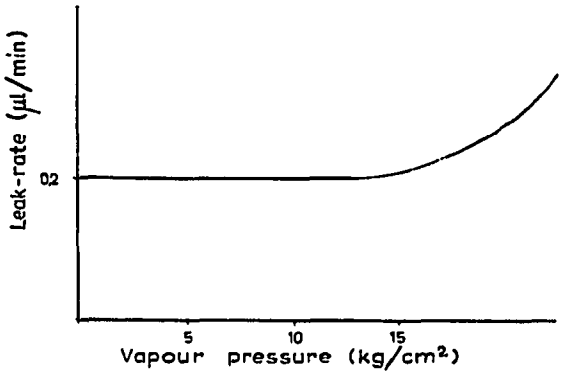

Fig. 7. Dependence of leak-rate on vapour pressure of sample.

by the graphical evaluation of recordings taken at high speed, using the method developed by Staszewski and Janák[17]. The chromatograms evaluated were recorded by a Brüel and Kjaer Type 2305 recorder, (Naerum, Denmark) (pen speed, 160 mm/sec; chart speed, 10 mm/sec). Using this recorder, distortion of peaks due to recording was made negligible.

In the course of the evaluation the areas under the peaks were divided into ten sections of equal height, and the ratios A_i/B_i (see Fig. 8) were plotted against the peak height (h). As shown by Fig. 8, the symmetry of the peak obtained by using the automatic sample-introducing system was better than that when using an injection technique.

In order to study reproducibility, ethanol was determined in 500 blood samples in the parts per thousand range using n-propanol as internal standard. On the basis of 500 measurements the reproducibility, σ, was found to be $\pm 0.94\%$.

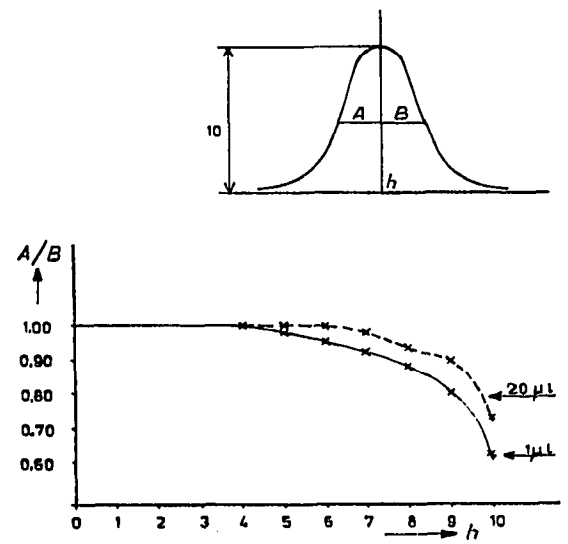

Fig. 8. Dependence of chromatographic peak shape on method of sample introduction. ———, Injection; — — —, introduction by boat.

TABLE I

RESULTS OF 20 PARALLEL MEASUREMENTS ON THE SAME SAMPLE

i	*Ratio of areas*		
	m_i	$m - m_i$	$(m - m_i)^2$
1	0.432	− 0.004	0.000016
2	0.435	− 0.001	0.000001
3	0.436	0.000	0.000000
4	0.442	+ 0.006	0.000036
5	0.444	+ 0.008	0.000064
6	0.444	+ 0.008	0.000064
7	0.436	0.000	0.000000
8	0.430	− 0.006	0.000036
9	0.422	− 0.014	0.000196
10	0.431	− 0.005	0.000025
11	0.436	0.000	0.000000
12	0.442	+ 0.006	0.000036
13	0.434	− 0.002	0.000004
14	0.438	+ 0.002	0.000004
15	0.436	0.000	0.000000
16	0.443	+ 0.007	0.000049
17	0.431	− 0.005	0.000025
18	0.436	0.000	0.000000
19	0.438	+ 0.002	0.000004
20	0.440	+ 0.004	0.000016

$m = 0.436$
$s\% = \pm 1.02$

In Table I results are presented of twenty parallel measurements made on the same sample. The percentage relative standard deviation, $s\%$, was ± 1.2.

Experience gained in the course of serial determination of alcohol in a great number of blood samples

The apparatus produced analytical results continuously, without any hindrance, although the requirements were rather strict from the analytical point of view and the results had to be produced 2 h after the arrival of the samples. After 20,000 analyses the apparatus was cleaned, which took 2–3 h. No specially trained staff was necessary to operate the apparatus.

DISCUSSION

In spite of the fact that the task of determining volatile constituents in slurries by GC occurs quite frequently, for example in process control, food chemistry, and environmental protection, the introduction of samples of this type into the gas chromatograph has been resolved to date neither from the theoretical nor the practical points of view, for reasons outlined at the beginning.

Vapour phase analysis seems to be best from the point of view of trouble-free running; however, the composition of the volatile fraction allowed to enter the column is essentially different from the original composition of the sample, the former being

a very complicated transformation of the latter. The advantage of the sample-introducing system described is that by modifying the method of vapour phase analysis the following disadvantages can be eliminated.

(1) The non-additivity of calibrations, even in the case of systems with ideal behaviour.

(2) Generally, the method of vapour phase analysis cannot be applied to real systems, *e.g.* due to the formation of azeotropic mixtures, etc.

(3) Interference caused by changes in the composition of the vapour phase, owing to adsorption phenomena or solvation.

The interferences mentioned were eliminated by shifting the equilibrium of the liquid and vapour phases in favour of the latter for the volatile constituents of the sample such that the effect of the liquid phase is negligible. In this way, the disturbances caused by the non-volatile matter in the samples could be eliminated by the appropriate construction of the sample-introducing system. The version described in the present paper operates semi-automatically, since there was no demand for full automation.

In constructing the sample-introducing system the requirements of GC were thoroughly considered, such as the minimization of dead volumes. This was ensured by incorporating the elements necessary for modified vapour phase analysis into the gas-flow switching tap. The control of the operational parameters of the latter was also part of the studies made on the sample-introducing system.

For comparison, in Table II the parameters are shown of the fairly good gas-

TABLE II

COMPARISON OF THE GAS-FLOW SWITCHING TAP DESCRIBED AND TWO COMMERCIAL ONES

Type	*Seiscor Dosierventil Model VIII**	*Pye Cat. No. 13440 gas-sampling valve***	*System described*
Mounting	Clamp type	Clamp type	Clamp type
Sample material	Liquid or gas	Liquid or gas	Slurry
Actuating air pressure, kg/cm²	2	2	2
Liquid sample size	Internal loop, 0.5 and 2 μl; other sizes on request	External loop; sample injection volume 0.3 to 25 ml	Internal loop, 8 and 28 μl, other sizes on request
Gas sample size, μl	25	—	—
Maximum operating temperature, °C	230	230	230
Leak-rate	Less than 1 μl/min	Max. leak-rate at 60 p.s.i.g., 4 kg/cm², 0.20 ml/min of helium	Less than 0.2 μl/min
Sample filter	5 μm recommended	Supplementary filter required	No supplementary filter required
Maximum operating pressure, kg/cm²	105	6.8	13
Construction	Stainless steel (other material on request)	Stainless steel (other material on request)	Stainless steel (other material on request)

* From the catalogue of Seiscor Division, Oklahoma City, Okla., U.S.A.
** From the catalogue of Pye-Unicam Ltd., Cambridge, Great Britain.

flow switching taps produced by two different firms and those of the system constructed by us. As shown by the data, our system is comparable in quality with the two types given. That is, increasing the functions of the system did not lead to a deterioration of the properties of the tap. In serial analyses of a great number of samples the determination time should be short. In some cases, such as the control of fast reactions, only high-speed chromatography or similar methods can be used successfully, regardless of the number of analyses to be done. High-speed GC places critical demands on sample introduction, so that distortion can be minimized. The system developed has remarkable properties from this point of view, and the experimental findings were fully verified by practical applications.

The splitting method developed has also advantageous features. In the usual splitting methods the system splits the gas stream according to the ratio requried. In our system, the two volumes are split after an equilibrium between the volumes is established. That is, the sample fractions in both spaces truly represent the original sample before splitting. This system is more sensitive to the amount of sample than the others, but the volume of the sampling space can be chosen according to the analysis to be performed to ensure optimum reproducibility of the sample amount. Thus the accuracy of measurements, as shown by the data in Table I, satisfies general analytical requirements.

Blood is a slurry which is very difficult to handle. The system constructed has been used for more than a year for determining alcohol in blood by GC. Various numbers of samples, the number not exceeding 150, are analysed each day for methanol, ethanol and acetone, using two or three parallel measurements. The task has been performed by using high-speed GC, the sample-introducing system described above, and a small computer[18]. *n*-Propanol was used as internal standard. Good separation of the four chromatographic peaks was achieved in 43 sec. At such a rate the analyses required per day could be obtained in a single shift.

Trouble-free operation on long runs verified the favourable properties of the system shown during the experimental period.

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