Notes

CHROM. 5400

A method of sampling by conventional syringes from moderately pressurized closed systems

It frequently happens that the content of a closed pressurized vessel has to be analysed by chromatography. Typical examples are cans or bottles containing beverages, spray containers, *etc.* The sampling from such a system as well as the sample transfer and its introduction into the analytical instrument (*e.g.* a gas or liquid chromatograph) may present serious difficulties, particularly when the content is a multiphase system. In such systems, the phases are mutually equilibrated, and any substantial change in the proportions of the phases will bring about appreciable changes in the proportions of the components that constitute the individual phases, except in few rare cases, such as a gas–liquid system in which the components have the same volatility.

Generally, if accurate quantitative analysis of any of the phases is to be performed, the amount of sample taken out of the container must be negligible in comparison with the total amount of the phase from which it is taken. In many cases this renders impractical the use of the devices that require the purging of the sampling section by larger amounts of the material being sampled.

Sampling from pressurized systems is an important problem in both gas and liquid chromatography, although many sampling systems have been described in this field[1–3]. The present paper describes a very simple procedure that permits the use of conventional syringes for taking representative liquid or gaseous samples from moderately pressurized containers and injecting them into the chromatograph.

Sampling procedure and the injection of the sample

The apparatus and the individual steps in sampling and sample introduction are illustrated schematically in Figs. 1 and 2. A silicone gum strip of about 20 mm in width and 4 mm in thickness is put around the container near the bottom and fastened by a collar made of a steel strip having its short end-pieces clamped and screwed together. In the middle of the steel strip there is a circular opening of about 7 mm in diameter. Before tightening the screws, a square cushion with an opening of the same size is inserted under the steel collar in such a way that both openings are situated concentrically. The cushion is made of a thicker metal sheet and is bent so that the radius of curvature is slightly larger than that of the container. Upon tightening up the screws, the cushion causes a local increase in the pressure of the rubber strip against the wall of the container, thus making the exposed region leak-proof. A small hole is than knocked through the rubber and container walls in the centre of the opening, using a sharp needle. When the needle is withdrawn, the hole remains closed by the rubber, but allows samples to be taken from inside the container.

The sampling is carried out in the following manner. First, a rubber plug of about 12 mm in length and 5 mm in diameter is fitted coaxially on the needle of the syringe and slid along the needle so that about 2 cm of bare needle tip are exposed.

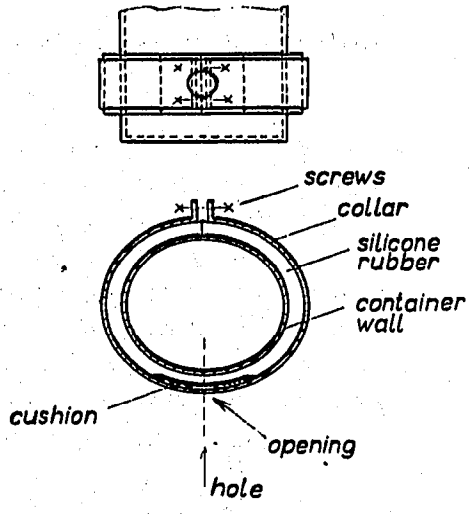

Fig. 1. Schematic diagram of the arrangement for the sampling.

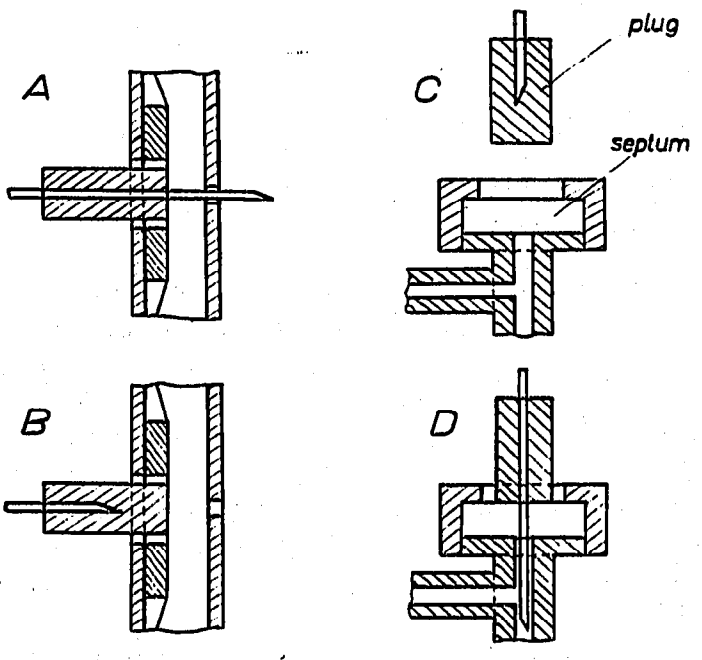

Fig. 2. Illustration of the steps in sampling and injecting the sample. A, introducing the sample into the syringe barrel; B, closing the sample in the barrel; C, transferring the sample; D, injecting the sample into the chromatograph.

This part of the needle is inserted into the hole made in the container wall, whereupon the barrel of the syringe is filled with the sample by operating the plunger (Fig. 2A).

The temperature of the syringe must not be higher than that of the container since it would be impossible to fill the syringe barrel due to a higher vapour pressure in the latter than in the container. The plug is then applied to the rubber membrane and the needle retracted until the tip reaches the centre of the plug (Fig. 2B). In this state, the sample may be easily moved without loss of liquid. If a small volume of the sample must be removed from the barrel (*e.g.* for making up solutions), this can be accomplished by simply forcing it out with the plunger; the hole left by the needle in the plug will allow the required liquid to pass through whilst being small enough to provide a leakproof closure when the plunger is stationary.

The injection of the sample into the chromatograph is carried out by applying the face of the plug to the inlet-port septum and inserting the needle. In most cases, the relatively high pressure in the barrel will force out the contents completely without the plunger being operated. The sample introduction is depicted in Figs. 2C and 2D.

Reliability of the method

The method has been tested by determining the reproducibility of sampling the liquid phase from a spray container pressurized by Freon 114 (1,1-dichlorotetrafluoroethane) and introducing the samples into a vial modified so as to represent the inlet port of a chromatograph. The vial contained a little charcoal covered by a glass-wool plug and was closed by a rubber serum cap representing the inlet-port septum. The sampling was carried out with a Hamilton 701-N syringe; fifteen 6-μl samples

were taken and injected into the vial, the sample amounts being determined by weighing the doses on a Sartorius 2400 balance. The average weight of a charge was 8.97 mg, and the standard deviation of a single measurement was 0.07 mg, *i.e.* the percentage coefficient of variation was 0.7.

The plot in Fig. 3 represents a comparison of the precision of the sampling and sample injection of the spray material by the present method with that of the conventional sampling and sample injection of a relatively non-volatile liquid. In both cases, the same injection syringe and weighing procedure were employed, tetrabromoethane being used as the sampled liquid in the latter case. The circular symbols are those obtained with tetrabromoethane[4] while the triangular symbol was obtained with the spray. It is evident from the position of the triangular symbol that the precision of the sampling and sample introduction of the spray material by the

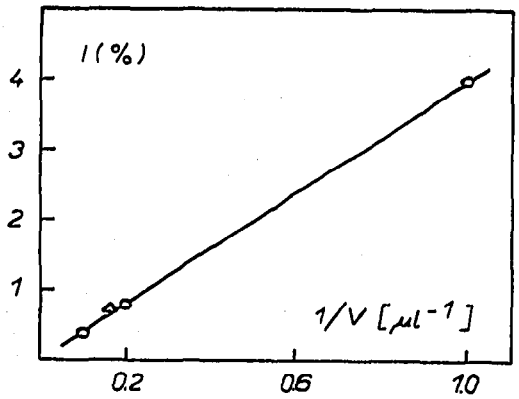

Fig. 3. Plot of the percentage coefficient of variation, $I(\%)$, of the volume sampled and injected *versus* the inverse of the volume, $1/V$. Circular symbols represent conventional sampling and injecting of tetrabromoethane with a Hamilton 701-N syringe. The triangular symbol corresponds to sampling and injecting by the present method with a syringe of a spray pressurized with Freon 114.

present method was almost the same as the precision of conventional sampling and injecting non-volatile liquids. In the case of the spray, the excess pressure inside the container and, consequently, in the syringe barrel when filled with the spray amounted to about 2 atm under the conditions of sampling.

Conclusions

The present method may be useful in the analysis by gas or liquid chromatography of canned beverages pressurized by carbon dioxide, sprays of cosmetic, medical, varnish, and other preparations, as well as liquids having appreciably high vapour pressures at ambient temperature.

If it is possible to define the total amount of the material in the container, the method provides for the use of the technique of internal standardization; the determined amount of the standard substance may be introduced into the container by an appropriate syringe prior to the sampling. For the analysis of the gaseous phase in a container, a Hamilton 1000 series syringe provided with a Hamilton GTS valve may conveniently be used without employing the plug in the sample transfer and introduction. However, any syringe suitable for the sampling of gases may be

used if only the relative proportions of the gaseous components are to be determined or if the pressure inside the container is measured.

The method may also be easily modified for sampling from bottles through the cap closure.

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