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Note

A simple device for the collection of gas chromatographic effluents from small-bore packed columns*

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In the past, we found it necessary to recover eluted compounds following the gas chromatographic (GC) analysis or purification of mixtures. This work included the preparative GC separation of isomers[1–5], to provide material for derivative formation and structural proof, collection and identification of compounds resulting from sample decomposition during chromatography[6] or recovery of fractions for additional instrumental examination[7,8] (IR, NMR, etc.). Many of these collections were carried out using the commercially available apparatus reported earlier[1–5]. Recently, however, the device shown in Fig. 1 has been designed and employed. The results obtained and some of the parameters that affect recovery efficiency are reported and discussed.

EXPERIMENTAL

Gas chromatography

An F & M Scientific Research Chromatograph, Model 5750 (Hewlett-Packard, Avondale, Pa., U.S.A.) equipped with a thermal conductivity detector (TCD; bridge current 150 mA) and coupled to an electronic integrator (Hewlett-Packard, Model 3370B) was used for all the GC analyses. A stainless-steel column (2 ft. × 1/8 in. O.D.) packed with 3.8% OV-17 on Chromosorb W, AW and DMCS-treated, 80–100 mesh, was employed. The carrier gas (helium) flow-rate was set at 25 ml/min. The injection port and column temperatures were kept at 210° and 130°, respectively, while the TCD temperature was varied as shown in Tables I and II. The sample size ranged from 1 to 5 μl during collection experiments and was standardized at 1 μl for quantitative analysis.

Sample collection and quantitative analysis

One-microlitre aliquots of each of the four compounds methyl Cellosolve, Cellosolve, *n*-butyl Cellosolve and *n*-butyl carbitol were injected separately at the different TCD temperatures shown in Table I. The collection device illustrated in Fig. 1 was connected to the exit port of the gas chromatograph for 1 min prior to sample elution. Separate recoveries of each of the above compounds were made

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TABLE I

RECOVERY EFFICIENCY OF GAS CHROMATOGRAPHIC EFFLUENTS AT DIFFERENT DETECTOR TEMPERATURES

Compound	*B.p.* (°C)	*Retention time (min)* *	*Recovery (%)*											
			Detector temperature (°C)											
			135				*170*				*230*			
			Wire out		*Wire in*		*Wire out*		*Wire in*		*Wire out*		*Wire in*	
			*RT***	*Cooled****	*RT*	*Cooled*	*RT*	*Cooled*	*RT*	*Cooled*	*RT*	*Cooled*	*RT*	*Cooled*
Methyl Cellosolve	124.3	0.2	86.5	97.9	87.0	99.3	82.3	98.9	90.0	100.9	52.2	62.2	51.5	69.9
Cellosolve	135.1	0.3	90.5	94.4	92.2	96.2	85.4	97.8	89.6	99.0	53.9	65.1	53.8	63.9
n-Butyl Cellosolve	170.6	0.4	–	–	–	–	97.0	97.4	94.5	100.1	92.2	99.2	95.5	102.0
n-Butyl carbitol	231.2	1.7	–	–	–	–	–	–	–	–	97.3	98.2	99.9	99.5

* Retention time of carbitol solvent = 1.2 min.

** RT = Collection device at ambient temperature.

*** Cooled = collection device cooled with liquid nitrogen vapour (−90 °).

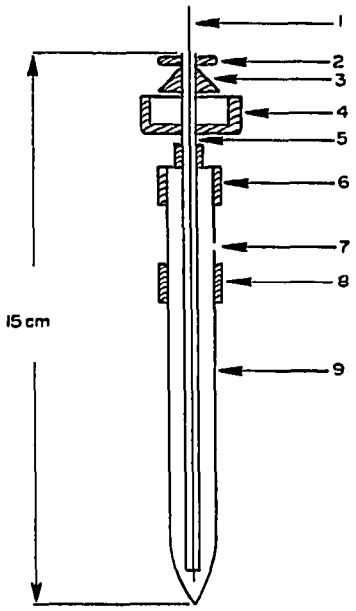

Fig. 1. Collection device assembly. 1 = Stainless-steel insert wire, diameter 0.018 in.; 2 = silicone rubber O-ring, 0.125 in. I.D.; 3 = Swagelok front ferrule, 1/8 in.; 4 = Swagelok nut, 1/8 in.; 5 = coagulation capillary tube, 6 in.; 6 = self-closing rubber stopper, sleeve type; 7 = pressure release vent; 8 = 1-cm length of rubber tubing, 1/4 in. I.D., 1/16 in. wall; 9 = sealed Pasteur pipette.

with the collector in four different modes: (1) at ambient temperature; (2) cooled with nitrogen vapour (−90°) (ref. 9); (3) at ambient temperature with wire insert; and (4) cooled with liquid nitrogen vapour and with wire insert. After peak elution, the collector was disconnected from the chromatograph and 50 μl of carbitol was added through the top end of the capillary tube. The piece of rubber tubing was slid over the vent and the entire assembly was centrifuged at 1500 rpm (g value, 1720) for 1 min. Approximately 1.5 in. of the tip containing the carbitol effluent solution was broken from the receiver. After thorough mixing of this solution, 1-μl samples were injected into the chromatograph for quantitative analysis.

Control samples, representing 100% recovery, were prepared by adding 1 μl of the appropriate Cellosolve or carbitol directly to the capillary tube of a collection device and treating it in the same manner as a recovered sample. All samples and controls were collected in duplicate, after which they were also analysed by duplicate injections. The recovery efficiency was determined by comparing the peak areas (provided by the electronic integrator) from a given sample with those of the corresponding control. The results are shown in Table I.

The above procedure was repeated for samples and controls of 2, 5 and 3×5 μl with the collector at ambient temperature without the wire insert. The results are shown in Table II.

TABLE II

RECOVERY EFFICIENCY OF GAS CHROMATOGRAPHIC EFFLUENTS FOR DIFFERENT SIZED SAMPLES

Collection device at ambient temperature.

Compound	*B.p.* (°C)	*Retention time* (*min*)*	*Recovery* (%)											
			Detector temperature (°C)											
			135				*170*				*230*			
			Sample size (*μl*)				*Sample size* (*μl*)				*Sample size* (*μl*)			
			*1***	*2*	*5*	*3×5*	*1***	*2*	*5*	*3×5*	*1***	*2*	*5*	*3×5*
Methyl Cellosolve	124.3	0.2	86.5	97.1	96.4	88.6	82.3	86.8	93.0	86.9	52.2	79.6	84.7	77.5
Cellosolve	135.1	0.3	90.5	100.2	94.9	87.8	85.4	85.3	92.3	93.6	53.9	80.3	89.8	82.2
n-Butyl Cellosolve	170.6	0.4	–	–	–	–	97.0	97.4	96.2	92.5	92.2	95.1	95.0	90.9
n-Butyl carbitol	231.2	1.7	–	–	–	–	–	–	–	–	97.3	100.0	99.7	99.2

* Retention time of carbitol solvent = 1.2 min.

** Values taken from Table I.

DISCUSSION

A large number and variety of collectors have been described in the literature, ranging from simple capillary tubes to elaborate coils and electronic precipitators. Among these have been devices with some similarity to the one shown in Fig. 1, that is, with a small-bore tube extending from the gas chromatograph exit port into a larger outer glass tube[10–12]. This design forces the sample-bearing carrier gas to travel a longer path before reaching the atmosphere, which in turn increases the efficiency of collection.

The collector shown in Fig. 1 is judged to possess several advantages. It is built from cheap materials that are readily available in most laboratories, virtually no skills, such as glass blowing, are required to assemble it and consequently the device can be made quickly by the user. The outer glass tube allows for repeated collections of a given GC peak or large injections, when greater amounts of sample are required such as for molecular structure investigations via derivative formation. Samples larger than 3 μl tend to be lost by blow-out when simple capillary tubes are used. The design lends itself to centrifugation and, because of its low cost and ease of construction, there need be no hesitation in sealing a sample in the tip for ampoule-type storage. For short-term storage, the unit is sealed by positioning the piece of rubber tubing over the pressure release vent and removing the capillary tube from the self-closing stopper. Connection to the Model 5750 gas chromatograph is simple, as the exit port of this instrument is equipped wth a 1/8-in. Swagelok fitting, while other instruments could be readily adapted.

The four compounds listed in Table I (methyl Cellosolve, Cellosolve, *n*-butyl Cellosolve and *n*-butyl carbitol) were chosen as test materials because they afforded a temperature range (> 100 °) from a moderate boiling point (124 °) to a rather high boiling point (231 °), which made it possible to examine the collection efficiency for a range of compounds at different detector temperatures. In addition, compounds boiling above 175 ° have long been noted for aerosol formation during collection[13], a feature which tends to make recovery more difficult.

There was a small decrease in the recovery of methyl Cellosolve and Cellosolve (Table I, collector at ambient temperature) when the detector temperature was increased from 135 ° to 170 °. A similar loss was noted for *n*-butyl Cellosolve when the detector was set at 230 °. In these instances, cooling (−90 °) overcame the minor losses. Recovery of both methyl Cellosolve and Cellosolve, however, decreased markedly at the higher detector temperature. The advisability of employing low detector temperatures during the collection of low-boiling effluents has been mentioned previously[14] and is demonstrated here. The detector temperature (as in Tables I and II) must be at least equal to or greater than the boiling point of the compound in order to eliminate possible condensation within the instrument. The results in Tables I and II suggest that the detector can be operated at approximately 50 ° above the boiling point of the collected compound without serious loss in recovery efficiency. Progressively lower recoveries should be expected if larger differentials between effluent boiling point and detector temperature become necessary.

Warming the capillary tube by pre-flushing (1 min) with carrier gas prior to sample collection serves a dual purpose. The air is removed, thereby protecting

oxygen-sensitive or hygroscopic samples from degradation or contamination and a gradual temperature gradient is developed to decrease aerosol formation. The wire insert was introduced in an effort to lengthen this temperature gradient, but the results in Table I indicate that the effect is small both at ambient temperature and at −90°, except for the collection of methyl Cellosolve at detector temperatures of 170° and 230°.

A means of producing a temperature gradient with a metal tube cover for capillary collectors has been reported[15]. This report, however, did not include results obtained when the metal cover was not used. Therefore, comparison of the effectiveness of a metal insert *versus* a metal cover, relative to a straight capillary cannot be made.

In order to simulate the experimental conditions that exist during the collection of a single fraction present in a group of closely eluting peaks, both methyl Cellosolve and Cellosolve were recovered (TCD temperature 170°) by connecting the collection device to the gas chromatograph just prior to peak elution. This procedure eliminated the formation of a temperature gradient and the collection efficiency was reduced by 10–15%.

Table II illustrates the effect of increasing the sample size. In almost all instances the 2- and 5-μl samples provided better collection efficiency than 1-μl and 3 × 5-μl samples. The reason for this behaviour was not established although there may be a regular initial loss. This would represent more on a percentage basis for the 1-μl samples and result in a lower recovery efficiency. Lower recovery efficiency for the 3 × 5-μl than for the 5-μl sample is probably due to the evaporation of previously recovered material during the collection of subsequent samples.

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