

RAPID DESORPTION-INJECTION SYSTEM FOR GAS CHROMATOGRAPHY  
OF PRECONCENTRATED HEADSPACE SAMPLES

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ABSTRACT

A desorption-injection apparatus providing a convenient inexpensive means to transfer preconcentrated volatile mixtures from a sorbent polymer trap onto a GC column without interruption of the operation of the gas chromatograph is described. Thermal desorption is accomplished by resistive heating of a stainless steel trap. Performance of the apparatus was evaluated with data from a known volatile mixture obtained by both desorption-injection and by direct injection.

INTRODUCTION

Preconcentration of the components of headspace, airborne, or aqueous volatile mixtures by trapping on a sorbent polymer

material prior to GC analysis, has become a common sampling technique<sup>1-3</sup>. The use of suitable sorbents for trapping avoids the concentration of water which adversely affects most GC column packings. Volatile components in a headspace are usually transferred by a stream of nitrogen or air to the sorbent polymer packed in a small bore glass tube. After the sample is collected the volatile mixture is transferred from the trap to a GC column. Several methods for transferring the sample into a gas chromatograph have been devised<sup>4-17</sup>.

The design objectives for the above methods consider thermal desorption from a trap and introduction of a sample onto the front of a column to be two separate operations. Usually the sample is trapped on a sorbent contained in a glass tube. Thermal desorption occurs when the glass trap is placed within a heated metal sleeve, a heating coil, or a modified injection port. The time for desorption can vary from 2 minutes<sup>17</sup> to 30 minutes<sup>9</sup>. Carrier gas flow subsequently carries the sample onto the analytical column with or without a cold trap as an intermediate step. Jacques and Morgan achieved rapid thermal desorption following sample pyrolysis by electrically heating a metal tube containing a quartz sample trap, although the sample is eluted into a cold trap before injection onto a column<sup>18</sup>. Melcher and Caldecourt also used direct resistive heating of a precolumn trap in designing a purge and trap system<sup>19</sup>. By combining rapid thermal desorption with carrier gas elution of

the volatile sample and redesigning the components, one can desorb and inject samples in one operation.

We have developed a more rapid, simpler, relatively inexpensive method for conveniently transferring samples from a sorbent polymer trap in which the trap itself becomes the resistive element in an electric heating circuit. We have used this apparatus to concurrently desorb and inject headspace samples of fruit aromas onto packed columns in less than 30 seconds without interrupting the operation of the gas chromatograph. Two versions of the device have been constructed and used with both Varian 2700 and 3700 instruments<sup>20</sup>. This device requires only a slight modification of the gas chromatograph.

## EXPERIMENTAL

### Apparatus

The desorption-injection apparatus consists of the components listed in Table 1. A schematic diagram is shown in Fig. 1. The four main elements of the apparatus are a sorbent trap, an electrical heating circuit in which the trap is a resistive element, a mounting bracket for the injection needle, and a preheater for the carrier gas<sup>21</sup>. Also required is a slight modification of the chromatograph to divert the flow of carrier gas through the desorption-injection assembly when necessary.

The sorbent trap consists of stainless steel tubing 23.3-cm long with a nut and ferrule on each end which is packed with any

TABLE 1

## Components and Material for Desorption-Injection Apparatus

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Mass flowmeter, 0-100 mL/min (Matheson, Model LF-100 with type E-100 sensor).
Normally closed two-way solenoid valve (Skinner Electric Valve Div., 115 vac, 6 watts, 1/16" orifice).
Normally open two-way solenoid valve (Skinner Electric Valve Div., 115 vac, 10 watts, 1/16" orifice).
Autotransformer—2 kilovolt-ampere (American Instrument Co., Type 4-803).
Two autotransformers—550 volt-ampere (General Radio Co., Variac, Type W5MT).
Finely stranded insulated cable, 6 gauge (automobile jumper cables).
Polymer sorbent material, 60-80 mesh.
Stainless steel tubing, type 316 or 304, 0.125 in. o.d., 0.009 in. wall . thickness, 23.3 cm length, with two 1/8 in. Swagelok fittings.
Carrier gas preheater—cylindrical copper block, 4 cm x 2 cm diameter stainless steel tubing, type 316, 1/16 in. o.d., 0.009 in. wall thickness. Swagelok fittings two brass adapters, 1/8 in. Swagelok to 3/16 in. tube. Two 1/8 in. type 316 stainless steel caps.
Needle bracket—copper, 1 x 3 x 3/32 in., bent into a right angle. Swagelok fitting—brass adapter, 1/8 in. Swagelok to 3/16 in. tube. No. 20 hypodermic needle.
Two heavy-duty copper clamps - 1-3/4 x 1 x 3/8 in.
Transite plate - 30 x 7.5 x 0.5 cm.
Iron-constantan thermocouple
Direct reading thermocouple gauge, 0°-250°C.
Multiple outlet box—three outlets with independent switches.
Stopwatch.
Silicone rubber septum material, 3/16-in. thick.
Copper refrigeration tubing, 1/8-in. o.d.

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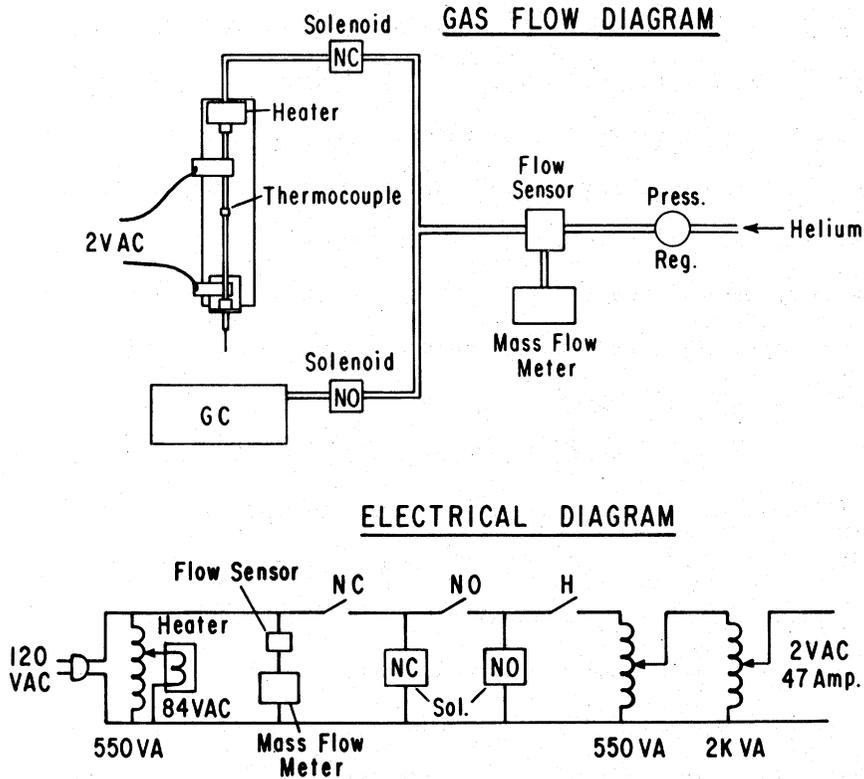


FIG. 1. Schematic of desorption-injection apparatus.

suitable sorbent. Glass-lined SS tubing can be used when necessary to maintain sample integrity. The length of the SS tubing determines the resistance of the trap heating circuit and the rate of trap temperature increase. The length can be varied to suit individual applications. Glass wool plugs secure the sorbent. Swagelok fittings connect the trap to the preheater and the needle bracket. The carrier gas preheater and the needle bracket mounted on a transite backplate (30 x 7.5 x 0.5

cm) for the chief mechanical assembly of the apparatus. The preheater (190°C) was designed in this laboratory and consists of a coil of stainless steel tubing around a small copper block containing a cartridge heater controlled by an autotransformer. The needle bracket is a small copper angle which is fitted with a Swagelok adapter and a short No. 20 needle. This bracket terminates the trap with the needle and provides one electrical connection to the trap.

The AC trap heating circuit, which provides a rapid increase in the temperature of the sorbent trap, is included in Fig. 1. The circuit carries 47 amps at 2 volts. Voltage control is provided by two autotransformers, 550 va and 2 kva. The heavy-duty electrical connectors to the sorbent trap are two copper clamps specially constructed for this purpose. Each clamp terminates a heavy-duty cable (automobile battery jumper cables) leading to a 2 kva autotransformer. One clamp attaches directly to the sorbent trap adjacent to the preheater. The other clamp attaches to the needle bracket.

The completed desorption-injection assembly provides a continuous heated carrier gas channel through the preheater, trap, and needle into the injection port. The distance between the two clamps determines the resistance of the trap heating circuit and thus the rate of temperature increase. An iron-constantan thermocouple senses the temperature of the trap assembly. The thermocouple junction is temporarily fastened to the trap

about midway between the electrical connectors with a small insulated clamp. A thermocouple gauge<sup>22</sup> calibrated in °C indicates the temperature. The temperature reading is a useful approximation of the actual temperature of the sorbent which is somewhat higher.

For use with a Varian 3700 the preheater, trap, and needle bracket assembly were suspended above the injection port. The assembly must be free to move vertically several inches from the injection port. This is readily accomplished with pulleys and a counterweight. For use with a Varian 2700 two lengths of aluminum angle were fastened to the front panel just below the injection port to accommodate the desorption-injection assembly.

#### Carrier Gas Flow Path

The carrier gas flows from a supply cylinder through a mass flowmeter sensor (or a suitable rotameter) to a branch point, as shown in Fig. 1. Between the branch point and the injection port there are two carrier gas channels. The main channel goes through the gas chromatograph, which has been modified. The carrier gas inlet line bypasses the instrument flow controllers and connects to the head pressure gauge. Flow in the main channel is determined by a normally open (NO) solenoid valve. The alternate channel goes through the desorption-injection apparatus, and the flow is determined by a normally closed (NC) solenoid valve<sup>23</sup>. System carrier gas pressure is controlled by the pressure regulator at the gas supply cylinder. All connec-

tions were made with 1/8-inch copper tubing and Swagelok fittings. The arrangement of the three electrical switches which control the trap heating circuit and the two solenoid valves is also shown in Fig. 1.

#### Desorption-injection Procedure

Connect a trap containing a volatile mixture to the pre-heater and the needle bracket. Close switch 3 so that the trap heating current will flow when switch 2 is closed. Move the desorption-injection assembly along the axis of the injection port until the needle point partially penetrates the 3/16-inch thick septum. Momentarily holding a spacer, 15/16 inch wide, at the injection port cap determines the length of travel of the assembly to the first position<sup>24</sup>. Embedding the needle point in the septum closes the outlet of the alternate carrier gas channel. Close switch 1 to open the NC valve. The mass flow-meter or rotameter shows a rapid increase in gas flow, followed by a slower return to the initial flow. The alternate carrier gas channel is now at operating pressure, while carrier gas still flows in the main channel.

Close switch 2 while moving the desorption-injection assembly toward the injection port. Thus, three operations occur simultaneously: the NO valve is closed, the trap heating circuit current flows, and the needle penetrates the septum. A projection on the backplate determines the length of travel of the assembly. The main carrier gas channel is now closed, and

DESORPTION-INJECTION SYSTEM

carrier gas is flowing through the alternate channel to the preheater. As carrier gas passes through the trap, desorption and elution begin immediately.

Open switch 3 a few seconds later at a predetermined temperature as indicated by the thermocouple gauge. The effect of temperature on the sample and/or the sorbent material determines the maximum allowable temperature for a particular application. For our use, the trap was packed with 70 mg of Tenax-GC. Careful timing is necessary (Fig. 2), because the indicated trap temperature continues to rise after the heating circuit is turned off. For example, if the trap temperature should not exceed 150°C, then the heating circuit is turned off when the thermocouple gauge indicates 100°C. For our use, we accurately counted a

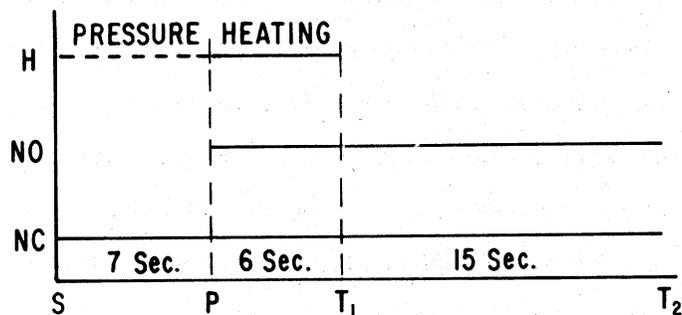


FIG. 2. Switching Program ---- and — indicates a switch is closed. Three switches are: NC for normally closed solenoid; NO for normally open solenoid; H for trap heating circuit. Specific times during the switching sequence are: S = close switches NC and H; P = alternate carrier gas channel is fully pressurized, and switch NO is closed; T<sub>1</sub> = trap temperature reaches 100°C, open switch H; T<sub>2</sub> = desorption-injection is complete, open switch NC.

15-second time period after the heating current is turned off as the indicated trap temperature increased rapidly to 150°C effecting desorption and elution of the sample into the injection port. The time period can be varied to suit the needs of the user.

The procedure ends as three operations again occur simultaneously; as the desorption-injection apparatus is withdrawn from the injection port, switch 1 is opened to return both solenoid valves to their original status. Carrier gas again flows in the main channel to the injection port. The sample is on the column, and the chromatograph continues in operation without interruption.

#### Estimate of Sample Recovery

A test mixture of p-cymene, (-) limonene,  $\alpha$ -phellandrene,  $\alpha$ -pinene, and ethyl acetate in carbon disulfide was prepared for the determination of sample recovery from the trap. The total solute concentration was approximately 10 mg/mL. The concentration of each component was approximately 2 mg/mL. The solution volume was sufficient to minimize the change in concentration because of evaporation during sampling. This solution was used for both direct injection into the gas chromatograph and application to the trap. For the latter, 1  $\mu$ l of solution was applied to the trap packing at the end normally connected to the needle bracket, using a 1  $\mu$ l zero dead volume syringe. Immediately after application, the end of the trap to which the

sample was applied, was connected to a nitrogen source giving a flow rate of 60 mL/minutes. After 10 minutes the nitrogen flow was stopped; the trap was disconnected, and the ends capped. Shorter time periods of nitrogen flow<sup>9</sup> were found to give variable results. The sample was then desorbed-injected into the gas chromatograph. Peak area data were obtained with an Infotronics CRS-11HSB electronic integrator. Repeated desorptions from the same trap were made until the total peak area of a single desorption was less than 1% of the accumulated area of all the desorptions.

### RESULTS

The desorption-injection apparatus was first used in a study of the composition of the aromas of intact fruits. For this purpose, two of these devices were constructed. One was used in a vertical arrangement with a Varian 3700 GC with simultaneous detection by flame ionization and Fourier transform infrared spectroscopy with a 1:3 effluent split ratio between the two.

The modification of the gas chromatograph is necessary, because the instrument flow controller cannot quickly reestablish the preset flowrate when carrier gas flow is diverted to the desorption-injection assembly. The slow recovery caused a deviation of the chromatogram baseline and distorted component peaks eluting during the first 3 to 4 minutes. The present design permits a rapid pressurization of the alternate carrier

gas channel without disturbing the existing flow to the separating column and permits a change in flow path with little change in carrier gas flow rate, minimizing baseline disturbance in the GC output. This is shown in Fig. 3, a chromatogram of the aroma of two Persian limes obtained with this system. The second apparatus was fitted in a horizontal arrangement to a Varian 2700 GC using mass spectrometric detection.

A quantitative measure of sample recovery was obtained with the test solution containing a mixture of five components likely to occur among the volatiles of intact fruit. Seven 1- $\mu$ l samples were directly injected into a Varian 3700 GC and five were applied to Tenax-GC traps followed by desorption-injection into the gas chromatograph. From the desorption-injection chromatograms an average HETP of 5.88 mm was calculated from the peak representing p-cymene. Direct injection of the same mixture onto the same column gave an average HETP of 4.55 mm. Direct injection data could not be used as a reference for estimating total sample recovery by desorption-injection, because the total peak area of desorbed samples was consistently higher than the average obtained by direct injection, where as much as 30% of the sample was lost on injection. This is probably due to injection port gas pressure forcing some of the sample solution back through the syringe along the clearance between the plunger and the needle, reducing the amount delivered to the gas chromatograph. Several syringes were tried

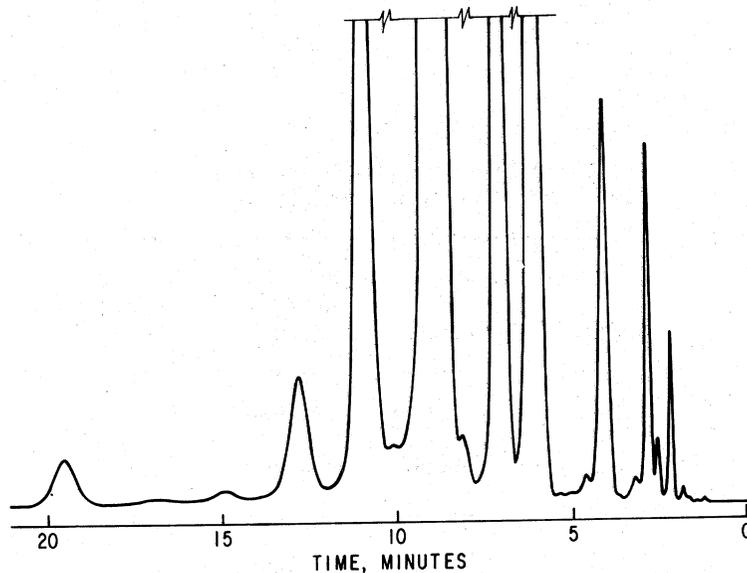


FIG. 3. Chromatogram of aroma of two lines.

with essentially the same result. On the other hand, prior to sample delivery our desorption-injection procedure equalizes the gas pressure in the trap with that of the chromatograph and prevents loss of sample. Assuming that all the sample present has been desorbed when the area of the last desorption-injection is less than 1% of the total, 90% or more of the sample was recovered on the first desorption-injection. The results are given in Table 2 which indicates the total sample recovery by desorption-injection and by direct injection. The total area count for a series of repeated desorption-injections from a given known sample was obtained by summing the five-peak area counts from all the chromatogram of the series. The amount of

Table 2.

Total Sample Recovery by Desorption-  
Injection and Direct Injection

Sample	Total <sup>a</sup> area count	First <sup>b</sup> Area count	Recovery <sup>c</sup> percent
1	503,000	496,000	98.6
2	441,000	434,000	98.6
3	453,000	406,000	89.8
4	565,000	557,000	98.6
5	505,000	486,000	96.2
Mean of desorption- injections	493,000	476,000	96.6
Direct <sup>d</sup> injection	343,734	-	-

<sup>a</sup> Sum of area counts for a series of repeated desorption-injections from a trap.

<sup>b</sup> Data for first desorption-injection from a trap, except last entry.

<sup>c</sup> Ratio of first area count to total area count.

<sup>d</sup> Mean of seven samples.

Table 3.

Comparison of Sample Composition:  
Desorption-Injection vs. Direct Injection

Sample	Composition—Area Percent				
	A	B	C	D	E
1	10.5	27.9	20.6	13.8	26.2
2	8.4	24.7	18.5	22.7	24.5
3	11.0	22.5	19.0	22.0	24.3
4	8.6	25.1	18.8	22.3	24.1
5	9.2	24.5	19.1	22.3	24.3
Mean of desorption- injection	9.5	24.9	19.2	20.6	24.7
Direct <sup>c</sup> injection	8.7	25.4	20.1	21.6	23.6

<sup>a</sup> Samples 1-5: Data for first desorption-injection from a trap. <sup>b</sup> A = Ethylacetate; B =  $\alpha$ -pinene; C =  $\alpha$ -phellandrene; D = (-) limonene; E = p-cymene. <sup>c</sup> Mean of seven samples.

sample recovered is stated as recovery percent which is the ratio of the sum of the five-peak area counts for the first desorption-injection of a series to the total area count for that series. For direct injection the total area counts of seven samples were averaged to give the value in Table 2. In

the case of compositional data, a comparison between direct injection and trap desorption-injection in terms of area percent is valid, and the data in Table 3 indicate that the agreement is good. One must keep in mind, however, that recovery depends on many factors such as attraction between sample and sorbent, volatility of the sample, trap temperature—which may be limited by the sorbent decomposition temperature, gas flow rate, and desorption time.

#### DISCUSSION

The desorption-injection apparatus provides a convenient, inexpensive means to transfer preconcentrated volatile mixtures from sorbent polymer trap onto a GC column without interrupting the operation of the gas chromatograph. Construction of the apparatus from readily available components and materials is straightforward. It is easily adapted to fit any gas chromatograph. The desorption-injection procedure is complete within 30 seconds and requires no separate or unusual sample handling techniques.

Heat for thermal desorption of volatile components is obtained by passing a high current at low voltage through the stainless steel tubing of the trap. The length of the metal tubing determines the resistance of the trap heating circuit and the rate of trap temperature increase. The desired maximum temperature for desorption for a particular application is determined by the length of time in seconds that the heating

current flows. Desorption and elution occur as the temperature within the trap rises rapidly. The thermocouple measures the temperature on the outer surface of the trap assembly which is a useful approximation of the actual desorption temperature. The heating current flows for a few seconds until a predetermined temperature lower than the desired maximum is indicated. The actual thermocouple temperature, at which the heating current is turned off, and the corresponding final trap temperature can be determined by a few practice runs. Desorption and elution continue until the desorption-injection apparatus is removed from the injection port, and the two solenoid valves are returned to their original status.

Volatile compounds are eluted most efficiently when the sorbent polymer packing begins about 1.7 cm from the needle bracket end of the trap. The electrical connection at that end of the trap is made through the needle bracket. Given the dimensions and the mass of the trap relative to the needle bracket, the end of the trap connected to the needle bracket may be slightly cooler. Placing the trap packing just beyond this point assures exposure to the desired temperature.

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20. Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.
21. Details of construction can be obtained by writing to the authors.
22. Assembly Products Inc., Chesterland, OH.
23. Skinner Electric Valve Div., New Britain, CT.
24. We used a small metal plate, which had one dimension equal to 15/16 inch, as the spacer.