

CHROM. 14,429

SYSTEMATIC ERRORS OCCURRING WITH THE USE OF GAS-SAMPLING LOOP INJECTORS IN GAS CHROMATOGRAPHY

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(Received September 29th, 1981)

SUMMARY

Gas sampling valves, involving a fixed-volume loop, are widely used as injection devices in gas chromatography. It is shown that adsorption of the substance under consideration on the inner wall of the loop tube will cause a systematic error in the injected amount. This effect can in many practical cases be significant as is shown by experiments and theoretical calculations.

INTRODUCTION

The simple arrangement of a sampling loop valve for gas-phase injections has been used in gas chromatography (GC) for a long time, and it has been described in most standard texts of gas chromatographic praxis^{1,2}. It makes use of a piece of tubing of known volume, which can be connected alternately to a sample gas stream and to the carrier gas stream. Such devices are offered as accessories to almost every type of commercial gas chromatograph. In process GC, this is the standard injection technique. Also in liquid chromatography³ and in flow-injection analysis⁴, similar arrangements are widely used.

When recently using a gas-sampling loop in an apparatus for measurements of gas-aqueous partition coefficients for hydrocarbons⁵, we noted systematically higher concentrations from analysis of the hydrocarbon gas stream using the loop injection compared with the concentration expected from the parameters of the generating apparatus. The latter agreed with measurements performed with other types of gas-phase analysis: injection with a gas-tight syringe and sampling via an adsorption tube.

It is clear that if the substance under consideration adsorbs on the inner wall of the loop tube when it is connected in the sample stream, it will desorb when clean carrier gas phase passes through. The result is an injection into the chromatograph of a larger amount of analyte than is expected from the volume of the tube and the gas-phase concentration. Should this effect be significant there is a systematic error, the

magnitude of which should depend on the tube material and geometry and on the sample type and concentration. No references to this problem were found in the literature.

As the precision of the injections with the loop injector is superior to that which is possible with other techniques, a systematic investigation of this phenomenon was performed.

In this work we report a simple theoretical treatment of the problem and some experimental data, showing that the effect is real and in practical cases often significant, especially for substances with low vapour pressures.

THEORY

As a model for the adsorption behaviour, we use the so called B.E.T. equation⁶:

$$\frac{x}{x_m} = \frac{c \cdot p/p_0}{(1 - p/p_0) [1 + (c - 1) \cdot p/p_0]} \quad (1)$$

where p is the partial pressure of the adsorbate, p_0 is its saturation vapour pressure, x is the amount adsorbed per unit area, x_m is the amount adsorbed in a monolayer of unit area and c is a constant. The amount of analyte, adsorbed on the inner wall of the sample loop is $x \cdot S_{\text{loop}}$ (S_{loop} is the inner surface area of the loop tube). Thus the relative error, f , caused by this adsorption is:

$$f = \frac{x \cdot S_{\text{loop}} \cdot R \cdot T}{p \cdot V_{\text{loop}}} \quad (2)$$

where V_{loop} is the volume of the loop, and R and T are the gas constant and absolute temperature, respectively. Ideal behaviour of the sample vapour is assumed. With eqn. 1 and the relation $V_{\text{loop}}/S_{\text{loop}} = r/2$, where r is the radius of the tube, we get:

$$f = \frac{x_m \cdot c \cdot 2 \cdot R \cdot T}{(1 - p/p_0) [1 + (c - 1) \cdot p/p_0] \cdot p_0 \cdot r} \quad (3)$$

For a given loop and vapour, eqn. 3 can be written:

$$f = \frac{d}{(1 - p/p_0) [1 + (c - 1) \cdot p/p_0]} \quad (4)$$

where d is a constant.

It can be seen that if $p = 0$ then $f = d$, and if $c > 2$ then f has a minimum value:

$$f_{\text{min}} = \frac{4d(c - 1)}{c^2} \quad (5)$$

at $p = 1/2 \cdot p_0 \cdot (c - 2)/(c - 1)$, approximately equal to $1/2 \cdot p_0$ at large values of c . Also, $f \rightarrow \infty$ when $p \rightarrow p_0$ (which is a hypothetical extrapolation, and does not apply

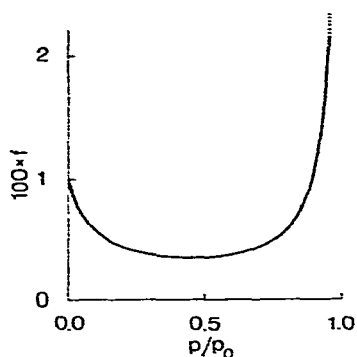


Fig. 1. Plot of f versus p/p_0 according to eqn. 4. Parameters: $c = 10$, $d = 10^{-2}$.

to the systems which were studied.) In Fig. 1, f is plotted versus p/p_0 in a typical case.

In principle it is possible to calculate the error which is made by using a sample loop from the equations given above. However, very few values of c can be found in the literature for systems of interest in this context. Thus it is possible only to give rough estimations of the effects involved.

CALCULATIONS

To calculate values of f from the equations given above, values of x_m are required. These were calculated from $x_m = 1/(\sigma \cdot N_A)$, where N_A is Avogadro's number and σ is the cross-sectional area of the adsorbate molecule, calculated by Hill's formula⁷, using critical constants readily available⁸. Saturated vapour pressures were calculated from Antoine equations given in ref. 8. The values found for these physical constants are summarized in Table I.

TABLE I
PHYSICAL CONSTANTS AT 25°C

Substance	p_0 (atm)	σ (\AA^2)	x_m (moles m^{-2})
Hexane	0.199	42	$4.0 \cdot 10^{-6}$
Benzene	0.123	32.5	$5.1 \cdot 10^{-6}$
Toluene	$3.75 \cdot 10^{-2}$	38.5	$4.3 \cdot 10^{-6}$
Ethylbenzene	$1.25 \cdot 10^{-2}$	41.3	$4.0 \cdot 10^{-6}$

EXPERIMENTAL

Sample vapour, generated with an apparatus, described earlier⁹, was pumped through a six-port valve to which were connected loops made of different materials and of varying size (see Fig. 2). The loops were kept at ambient temperature, and protected against draughts by a polystyrene insulation. In position A, clean nitrogen passed through the loop and further to a gas chromatograph (Hewlett-Packard, Model 402, Avondale, PA, U.S.A.) equipped with a Porapak P column (Waters Assoc., Milford, MA, U.S.A.); a flame ionization detector and a digital integrator.

(Infotronics, Model CRS 101, Shannon Airport, Ireland). In position B of the valve, the sample vapour passed through the loop. Samples were injected by switching the valve to position B for a defined period of time (see below) and then back to position A. The area of the resulting peak is denoted A_{loop} .

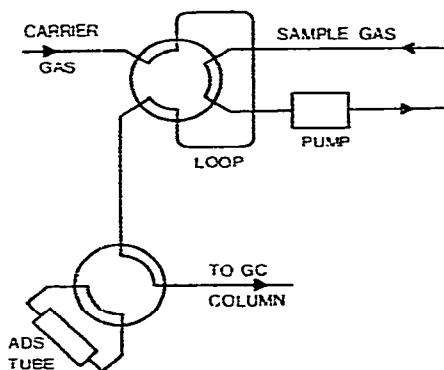


Fig. 2. Experimental arrangement.

Also, as a reference measurement, the vapour was sampled by adsorption on a porous polymer (Porapak Q, Waters Assoc.). Using a gas-tight syringe, a known volume of vapour, V_a (5–10 ml) was drawn through a tube (50 × 3 mm I.D.) filled with the polymer. The tube was connected to a four-port valve (see Fig. 2), and the adsorbed sample was thermally desorbed into the same gas chromatograph as the sample from the loop, giving the peak area A_a . The parameters of this analysis, such as desorption time and temperature, vapour volume and speed of sampling, were determined individually for each substance, and the sampling efficiency and recovery were checked as described below.

A quantity F , expressing the difference between the amounts of substance sampled in the two different ways, was calculated from eqn. 6:

$$F = \frac{A_{loop} \cdot V_a}{A_a \cdot V_{loop}} - 1 \quad (6)$$

RESULTS AND DISCUSSION

Measurements were performed with four substances using three different loops. The results, expressed as F values according to eqn. 6 are summarized in Table II. The uncertainty of the F values is *ca.* 0.03. To compare the experimental results with the theory, values of d (the maximum value of the expected error f), f_{min} (the minimum value) and $f_{0.01}$ (the value of f at $p/p_0 = 0.01$) were calculated for the current values of r and for different values of c . This is presented in Table III.

According to the very sparse literature data^{10,11}, c for hexane and benzene when adsorbed on clean glass or SiO_2 is *ca.* 10. From the tables it can be seen that a value of c *ca.* 100 (*i.e.* stronger adsorption) gives a better agreement with the experimental results for the GLT loop and the glass loop. For toluene and ethylbenzene, c values between 10 and 100 seem to give the observed effects. With the copper loop a very high adsorption was observed, corresponding to a c value of *ca.* 1000, which

TABLE II
EXPERIMENTAL RESULTS

Loops: GLT, glass-lined stainless-steel tubing, $r = 0.35$ mm, length 300 mm; glass, glass tube, with short copper connections, $r = 1.5$ mm, length 108 mm; Cu, copper tube, $r = 1.0$ mm, length 180 mm.

Substance	p/p_0	F	Loop
Hexane	$7.3 \cdot 10^{-4}$	0.16	GLT
	$9.0 \cdot 10^{-3}$	0.25	GLT
	$1.1 \cdot 10^{-2}$	0.25	GLT
	$5.0 \cdot 10^{-2}$	0.26	GLT
	$7.3 \cdot 10^{-4}$	0.05	Glass
	$9.0 \cdot 10^{-3}$	0.11	Glass
	$1.1 \cdot 10^{-2}$	0.11	Glass
	$5.0 \cdot 10^{-2}$	0.08	Glass
Benzene	$2.2 \cdot 10^{-2}$	0.20	GLT
	$7.0 \cdot 10^{-3}$	0.23	GLT
	$2.0 \cdot 10^{-2}$	1.5	Cu
Toluene	$2.3 \cdot 10^{-2}$	0.35	GLT
	$6.5 \cdot 10^{-3}$	0.33	GLT
Ethylbenzene	$2.9 \cdot 10^{-2}$	0.53	GLT

probably is caused by charge-transfer interactions (applicable with the aromatics only).

These comparisons can be made only half-quantitative owing to the uncertainties involved: the nature of the glass (especially the metal content of the GLT lining), the possibility of small cracks in the GLT lining, the presence of short copper connection tubes (attached with shrinkable PTFE) on the glass loop, the applicability of the B.E.T. equation to these systems (especially at lower pressures), the scantiness of literature data applicable to this problem, and the experimental uncertainty.

TABLE III
CALCULATED VALUES

Substance	c	r (mm)	d	f_{min}	$f_{0.01}$
Hexane	10	0.35	0.028	0.010	0.026
	100	0.35	0.28	0.011	0.14
	100	1.5	0.065	0.003	0.033
Benzene	10	0.35	0.058	0.021	0.054
	100	0.35	0.58	0.023	0.29
	100	1.0	0.20	0.008	0.104
	1000	1.0	2.04	0.008	0.188
Toluene	10	0.35	0.16	0.058	0.148
	100	0.35	1.60	0.063	0.81
Ethylbenzene	10	0.35	0.45	0.161	0.41
	100	0.35	4.47	0.177	2.27

By variation of the time during which the sample gas stream passed through the loop, rough information about the kinetics of the process was obtained. The peaks increased in size with this time, up to a limiting value which was reached after *ca.* 5 sec for the GLT loop, 15 sec for the glass loop and 60 sec for the copper loop. These times, which were used for the measurements of F , are much longer than what is needed to flush the loop with the gas, which is an additional indication that the adsorption indeed takes place.

The reference analysis, by adsorption on porous polymer and subsequent thermal desorption, was thoroughly checked. Two identical adsorption tubes were connected in series during the adsorption step. The second tube gave no peak at desorption. Various volumes of gas were drawn through the adsorption tube. The resulting peak areas formed, when plotted *versus* volume, a straight line through the origin. Different flow-rates were used with no significant difference. Also, some experiments were made with an adsorption tube containing Tenax-GC, with the same results as with Porapak Q. Two successive desorptions on the same tube showed that the desorption was complete. These experiments show that both the adsorption and desorption steps are performed with full efficiency, and the procedure can be trusted to give a result which is free of major systematic errors.

The adsorption in the six-port valve itself is negligible, as shown by the following experiment: another loop made from the same GLT tubing as the one which was used in most experiments, but shorter, gave peak areas which were smaller by the same factor as between the lengths of the tubes.

CONCLUSIONS

We have shown that systematic errors due to adsorption of the sample on the inner walls of gas-sampling loops can occur and will in many cases be significant and seriously influence the accuracy of this type of gas analysis. The error is most important for less volatile substances and for low concentrations. To decrease the errors, the loop should be made from an inert material and calibrations with known gas concentrations (approximately equal to that of the sample) should be made. The loop might be heated, to increase the vapour pressure. In that case, the gas stream should be preheated to the same temperature to avoid errors from expansion effects.

The precision (repeatability) of this injection technique is not impaired by the adsorption if the gas stream is flushed through the tube for long enough to allow the adsorption equilibrium to be completely attained.

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