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Note

The re-injection method for recovery of components adsorbed during syringe gas sampling: a statistical evaluation

CONSTANTINE DUMAS
Chemical Engineering Department, Queen's University, Kingston, Ontario K7L 3N6 (Canada)
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When sampling gases with a syringe, some of the sample may be lost by adsorption on the syringe barrel. This is particularly troublesome when mixtures are sampled, because certain components may adsorb more readily than others and this changes the composition of the sample.

In a previous investigation[1], a successive re-injection method was developed for recovering moisture adsorbed from water vapour samples. At that time, it was shown that the re-injection method produced a linear calibration curve and successive re-injections recovered a significant amount of the sample. However, certain questions concerning this method remained unanswered, because as discussed by the authors, a suitable calibration curve, for such low levels of moisture, could not be obtained by other methods. Therefore, although the water calibration curve was linear, the re-injection method could not be tested for systematic errors.

In this investigation, the re-injection method was used for the analysis of acetone vapour and a comprehensive statistical evaluation of the method was carried out. The analysis of acetone vapour, as opposed to water vapour, facilitates this evaluation for a number of reasons: (1) acetone peaks are less susceptible to tailing, (2) a flame ionization detector can be used with acetone, resulting in improved sensitivity and no interference from air and water peaks, and (3) standard, dilute solutions of acetone can be easily prepared, to allow gas chromatographic (GC) calibration by an alternate method. Comparison of the acetone vapour calibration to an acetone solution calibration is particularly useful, because adsorption does not occur with liquid samples.

EXPERIMENTAL

A Varian 3700 gas chromatograph with a flame ionization detector was employed. The column (0.4 m × 3 mm I.D., nickel) was packed with Porapak R (100–120 mesh). With helium as the carrier gas at a flow-rate of 30 ml/min and an oven temperature of 140°C, the retention time of acetone was 41 sec. Peaks were integrated with a Hewlett-Packard 3390A integrator.

Saturated acetone vapour, of known composition, was obtained by partially filling a 1000-ml flask with 300 ml of acetone, and maintaining it at 19.8°C in a constant temperature bath. The liquid standard was prepared by blending known volumes of acetone and distilled water.

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Vapour analysis was performed as described previously[1]. The desired volume of vapour sample was drawn into the syringe and then injected into the chromatograph. Then a volume of carrier gas equal to the sample volume was immediately drawn, and the syringe was left in the injection port. Once the acetone peak had been integrated, the syringe contents were re-injected into the chromatograph. This re-injection procedure was repeated three times.

A 50-μl liquid syringe, fitted with a Chaney adaptor, was used for liquid samples.

RESULTS AND DISCUSSION

The chromatograph was calibrated with acetone vapour using four injections per determination. Table I shows the effect of the number of successive re-injections on sample recovery (relative to the total amount of sample recovered with four injections) and precision for sample volumes of 10.0, 20.0, 30.0 and 40.0 μl. For each sample volume, ten replicate determinations were performed, each requiring four injections. Therefore, each mean response value in Table I has nine associated degrees of freedom. In all cases, no more than 92% of the total sample could be recovered with a single injection. The recovery continually increased with more re-injections, however in most cases, 99% or more of the sample was recovered using two injections. For example, with a 30-μl sample volume, the recovery increased from 89.1 to 99.3 and 99.9% for 1, 2 and 3 injections, respectively.

TABLE I

SATURATED ACETONE VAPOUR CALIBRATION DATA

a.u. = Arbitrary units.

Sample volume (μl)	*Acetone mass (μg)*	*No. of injections*	*Mean GC response* (a.u.)*	*Coefficient of variation* (%)*	*Recovery** (%)*
10.0	6.1	1	856 678	2.64	82.5
		2	1 011 979	2.58	97.4
		3	1 034 475	2.58	99.6
		4	1 038 613	2.57	100
20.0	12.2	1	1 815 640	1.23	88.2
		2	2 037 898	0.68	99.0
		3	2 056 294	0.64	99.9
		4	2 059 191	0.64	100
30.0	18.3	1	2 741 700	0.66	89.1
		2	3 055 317	0.46	99.3
		3	3 074 523	0.51	99.9
		4	3 077 148	0.52	100
40.0	24.4	1	3 704 990	2.31	91.3
		2	4 038 882	0.64	99.6
		3	4 055 005	0.57	99.9
		4	4 057 080	0.57	100

* Based on ten determinations.

** Recovery relative to four injections.

TABLE II

ACETONE SOLUTION CALIBRATION DATA

a.u. = Arbitrary units.

Sample volume (μl)	*Acetone mass (μg)*	*Mean GC response* (a.u)*	*Coefficient of variation* (%)*
0.20	6.1	909 348	8.39
0.40	12.2	1 889 190	3.52
0.60	18.3	3 063 280	3.83
0.80	24.4	3 976 320	7.02

* Based on 10 determinations.

The amount of sample loss resulting from sorption (with a single injection) was not constant. As the sample volume ranged from 10.0 to 40.0 μl, the single vapour injection recovery ranged from 82.5 to 91.3%. The precision, or reproducibility, of analyses can be quantified by the coefficient of variation, which is defined as: (standard deviation/mean) × 100%. The precision of determinations was poorest, in all cases, when using a single injection. More injections resulted in greater precision with the most significant improvement being realized using two injections. For example, using a 40.0-μl sample volume, the coefficient of variation decreased from 2.31 to 0.64, 0.57 and 0.57 with 1, 2, 3 and 4 injections, respectively (Table I). Therefore, in most practical situations, two acetone vapour injections would give adequate precision and recovery.

Various volumes of the standard acetone solution were selected for analysis such that the mass of acetone per sample was comparable to that of the vapour standards (Table I). Ten replicate analyses were performed for each liquid volume. Therefore, the mean response values of Table II each have nine degrees of freedom. Vapour sampling was significantly more precise than liquid sampling. The coefficient of variation ranged from 3.52 to 8.39% for liquid samples (Table II) compared to 0.46 to 2.58% for two injection vapour samples (Table I), with similar masses of acetone.

TABLE III

COMPARISON OF WEIGHED LEAST SQUARES REGRESSION PARAMETERS FOR VARIOUS CALIBRATION METHODS*

a.u. = Arbitrary units.

Calibration method	*Slope (a.u./μg)*	*Intercept (a.u.)*	*Correlation coefficient*
Acetone solution	$172 \cdot 10^3 \pm 7 \cdot 10^{3**}$	$-17 \cdot 10^4 \pm 8 \cdot 10^{4**}$	0.9905
Acetone vapour (one injection)	$155 \cdot 10^3 \pm 2 \cdot 10^{3**}$	$-8 \cdot 10^4 \pm 2 \cdot 10^{4**}$	0.9991
Acetone vapour (two injections)	$166 \cdot 10^3 \pm 1 \cdot 10^{3**}$	$1 \cdot 10^4 \pm 2 \cdot 10^{4**}$	0.9998

* Each calibration method has 38 associated degrees of freedom.

** 95% confidence interval.

The mean response values of Tables I and II were used to compute three calibration curves for acetone solution, single injection vapour and two injection vapour standards. Because the pure error variance was not independent of sample volume, as reflected by the coefficient of variation values of Tables I and II, ordinary linear regression of the calibration data would not be valid. Therefore, weighted linear regression had to be applied, whereby each value was weighted inversely proportional to its pure error variance. The pure error variance, and thus the weights, were computed from replicate determinations. The resulting regression parameters for each of the calibration curves are compared in Table III. Of these, the two injection vapour calibration curve was the most linear, with a correlation coefficient of 0.9998. Also, it passed closer to the origin than the other two calibration curves and in fact, was the only curve with an intercept value that (within 95% confidence limits) passed through the origin. The slope of the single injection acetone vapour calibration curve was significantly lower than the other two, indicating sample loss. However, within 95% confidence limits, there was no significant difference between the sensitivity of the acetone solution and the two injection acetone vapour calibrations, as indicated by slope values of $172 \cdot 10^3 \pm 7 \cdot 10^3$ and $166 \cdot 10^3 \pm 1 \cdot 10^3$ for the acetone solution and the two injection acetone vapour curves, respectively. This similarity in sensitivity indicates that the re-injection method does in fact completely recover adsorbed sample components and is free of systematic errors.

CONCLUSIONS

Of the calibration methods investigated, the re-injection vapour method produced the best calibration curve. Statistically, it was the most linear and was the only curve that passed through the origin. The single injection method exhibited significant sample losses. By comparison with the liquid standard calibration curve, it was shown that the re-injection method was free from systematic errors and resulted in complete recovery of adsorbed components.

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REFERENCE

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