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METHOD FOR THE PREPARATION OF CONTINUOUS STREAMS OF GASEOUS CALIBRATION MIXTURES WITH DEFINED CONTENTS OF STANDARD SUBSTANCES

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SUMMARY

A method for the preparation of gaseous calibration mixtures with defined contents of standard substances is described. An accurately controlled stream of gas (*e.g.*, nitrogen) is drawn at a low flow-rate through a thermostated container filled with a chromatographic support impregnated with the standard substance, thus generating a continuous stream of saturated vapour of the substance. This stream is diluted in a mixing chamber with a large stream of pure gas, and a small fraction of the dilute mixture, separated by means of a splitter, is again diluted with a large stream of pure gas in another mixing chamber. In this two-stage dilution procedure it is possible to prepare mixtures containing standard substances at parts per billion concentrations with an error of about 4%. Mixtures containing several standards are obtained through use of a separate saturator for each standard; the concentration ratio of two standard substances can be set to within the range 1:1 to $1:10^6$.

INTRODUCTION

In developing and/or testing gas chromatographic methods, there often arises the problem of the preparation of gaseous calibration mixtures with a defined concentration of standard substances. Usually, mixtures with low contents of substances the saturation vapour pressures of which are lower than atmospheric pressure at ambient temperature are involved. These mixtures are prepared in essentially two ways: by static and by dynamic methods.

Static methods consist in the introduction of defined amounts of standard substances into a known volume of gas under specified conditions of state. These methods have the advantages of usually a simpler experimental arrangement and a relatively easy preparation of mixtures containing several standards. On the other hand, they give only a limited amount of the mixture, and the procedure may be complicated by the necessity to eliminate the effects of spurious adsorption of substances on the walls of the container and/or the errors incidental to measuring out very small amounts of the substances to be charged into the container. An example

of applying such a method is the work of Yoon and Pierce[1], who prepared gaseous mixtures containing about 0.05 ppm of C_5 and C_6 hydrocarbons.

With the dynamic methods there is generated a continuous stream of a gaseous mixture containing a certain fraction of the standard substance. If necessary, this mixture can be further diluted with a stream of pure gas. The composition of the primary stream is realized in essentially four ways, namely: (i) by drawing a stream of pure gas through a layer of the liquid standard substance in a container, *i.e.*, by saturating the gas with the vapour of the substance[2–6]; (ii) by a defined diffusional flux of the standard substance into a stream of gas[7–13]; (iii) by permeation of the standard substance through a membrane into a stream of gas[14,15]; and (iv) by continuously dosing the standard substance directly into a stream of gas[16]. Lovelock[12] described a method based on the use of the so-called exponential cell; a preliminary prepared gaseous mixture of a given initial composition is continuously diluted in a mixing chamber with a steady stream of pure gas. Bruner *et al.*[17] employed a combination of a permeation tube and an exponential cell. Fowlis and Scott[19] employed a dilute solution of a volatile substance of a given initial concentration in a non-volatile solvent to saturate a stream of gas with the volatile compound by exponential dilution.

In this paper, a procedure for the preparation of continuous streams of gaseous calibration mixtures is described, based on saturating a small stream of gas with the vapour of the standard substance being deposited on an inert chromatographic support and diluting, in a defined manner, the saturated gas with a large stream of pure gas. This procedure is especially advantageous for studying gas chromatographic methods in trace analysis. The reasons why we chose a saturation method are as follows: (1) the resultant concentration of the standard substance in the gas can be calculated exactly from the saturation vapour pressure of the substance and the flow-rates of the gas; hence, after it has been checked that the apparatus is functioning properly, it is not necessary to carry out calibrations; (2) mixtures with two or more standards can be prepared through the use of the corresponding number of saturators; and (3) the concentrations of standards in the resultant mixture are functions of several parameters (temperature of the saturators, gas flow-rates through the saturators, flow-rates of dilution gases) which can be varied within wide limits, thus making it possible to prepare mixtures containing several standards with their relative proportions being variable over a range of several orders of magnitude. This is very important, for instance, in studying interference effects in trace analysis by enrichment methods.

APPARATUS AND PROCEDURE

A schematic diagram of the complete apparatus is shown in Fig. 1. Pure nitrogen from a cylinder with a double reduction valve is dried in a tube (1) packed with molecular sieve 5A. The outlet of the tube is split into three and/or more (with more saturators) parallel branches in which the gas flow-rates are controlled independently by fine needle valves (2). In the branches comprising rotameters 5 and 6 the gas passes through tubes (4) filled with molecular sieve 5A and activated carbon. As the apparatus works on the principle of direct dilution of saturated gas with pure gas, it is advantageous, considering the necessary absolute flow-rate of the dilu-

ting gas and its overall consumption, to work with as low flow-rates as possible through the saturator; in this work these flow-rates were in the range 0.2–1.5 ml/min. It is very difficult to control accurately such low flow-rates by a needle valve, and a capillary splitter (3) was therefore installed in the saturation line in order to increase the regulated flow of the gas through the needle valve. The flow meters (7) were differential manometers of the usual construction, sensing the pressure drop across a capillary. The measuring capillaries of the flow meters were drawn from glass tubes on the instrument described by Desty *et al.*[18]. In order to improve their mechanical strength, the capillaries were surrounded by epoxy resin in glass tubes. From the flow meter the gas is led into the saturator (13), the latter being placed in a water thermostat (8) which maintains a constant temperature with a precision of $\pm 0.02°$. More detailed illustrations of the individual parts of the apparatus are given in further figures.

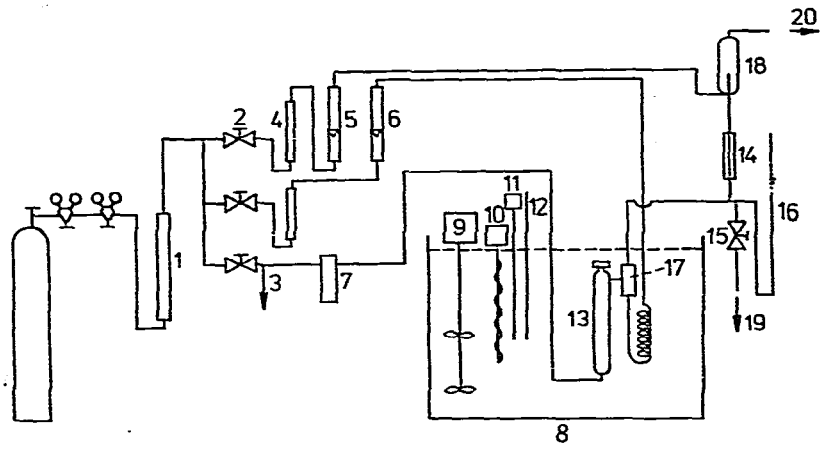
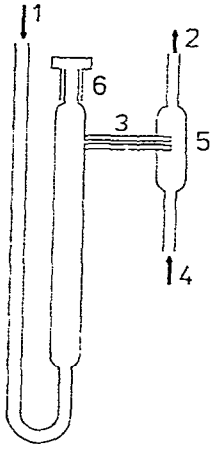


Fig. 1. Schematic diagram of the complete apparatus. 1 = Tube with molecular sieve; 2, 15 = needle valves; 3 = capillary; 4 = tubes with molecular sieve and activated carbon; 5 and 6 = rotameters; 7 = capillary flow meter; 8 = thermostated vessel; 9 = agitator; 10 = heater; 11 = regulating thermometer; 12 = measuring thermometer; 13 = saturator; 14 = capillary; 16 = manometer; 17, 18 = diluters; 19, 20 = outlets.

The saturator proper is shown in Fig. 2. It consists of a glass U-tube, the broader shoulder of which is provided with a removable closure (6). The gas coming from the flow meter enters the saturator at position 1, percolates through the saturator packing and, saturated with vapour of the standard, is led via capillary 3 (about 0.6 mm I.D.) into diluter 5. In this diluter the saturated stream is mixed with the stream of pure gas coming from rotameter 6 (Fig. 1) and entering the diluter at position 4, and the mixture leaves the diluter at position 2. The saturator was packed with Chromosorb P (60–80 mesh) (about 5 m^2/g) impregnated with 30–40% (w/w) of the standard substance. The impregnation was carried out without using any solvent, *i.e.*, the support was mixed directly with just the amount of the standard substance that would still give a loose material. In the first dilution stage, mixtures can be obtained with concentrations of the standard substance of a few parts per million.

The mixture leaving the above diluter enters at position 1 another diluting unit, shown schematically in Fig. 3. In this unit use is made of a capillary splitter, consisting of capillary 4 and needle valve 5. The capillary again has dimensions suit-

able for low flow-rates, and the pressure drop across the capillary, ΔP, is measured by manometer 7. The flow-rate of gas through the capillary, proportional to the pressure drop ΔP, is set by valve 5. A major part of the gas mixture is discharged through the valve into the atmosphere (position 3). The stream leaving capillary 4 is again mixed in diluter 8 with a stream of pure gas, coming from rotameter 5 (Fig. 1) and entering the diluter at position 2. The resultant mixture flows via a practically resistance-free insert (9) of glass beads into the atmosphere (position 10). In this second dilution stage, mixtures can be prepared with the standard substance in concentrations of a few parts per billion. With two or more saturators connected in parallel in the above arrangement, it is possible to prepare mixtures with comparable proportions of the individual standard substances.



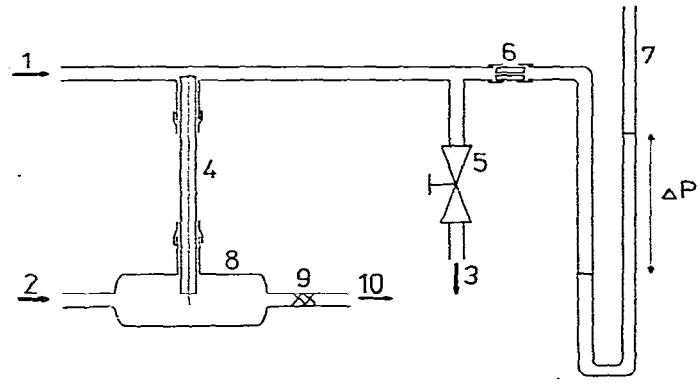


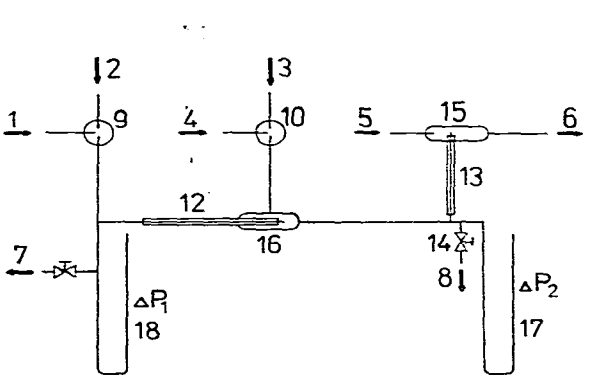
Fig. 2. Saturator. 1, 4 = Inlets; 2 = outlet; 3 = capillary; 5 = diluter; 6 = closure.

Fig. 3. Detailed diagram of the diluter with the capillary splitter. 1, 2 = Inlets; 3, 10 = outlets; 4 = capillary; 5 = needle valve; 6 = capillary junction; 7 = manometer; 8 = diluter; 9 = insert of glass beads.

The preparation of mixtures with substantially different concentrations of two standards is illustrated in Fig. 4. Diluter 9 is entered at position 1 by a stream from a saturator and at position 2 by a diluting stream. The effluent from diluter 9 is split in the above-described way; the pressure drop across capillary 12 is given by the difference between the pressures shown by manometers 18 and 17. Capillary 12 leads into diluter 16, into which there also leads the outlet of the diluter (10) processing a stream from the second saturator. The mixture leaving diluter 16 is again split; the pressure drop across capillary 13 is measured by manometer 17. Capillary 13 leads into diluter 15, in which the entering mixture is diluted with a stream of pure gas supplied at position 5. The resultant mixture leaves the unit at position 6.

Fig. 5 shows a modification of the apparatus which can be employed advantageously when it is necessary for the ratio of the concentrations of two standards to be varied while keeping the concentration (usually low) of one of the standards constant. At positions 3 and 5 there are supplied into diluter 1 a stream from a saturator and a diluting stream, respectively, and the effluent mixture, being split in the above-described way, is led via capillary 9 into diluter 10. The pressure drop

across capillary 9 is measured by manometer 7. The concentration which is to be maintained invariant is controlled by setting the flow-rate of the diluting stream supplied at position 6 into diluter 2. At position 4 there is supplied a stream from the second saturator. The flow-rate of this stream is set so as to make it negligibly small in comparison with the diluting stream supplied at position 6. All of the U-tube manometers were filled with a silicone oil.



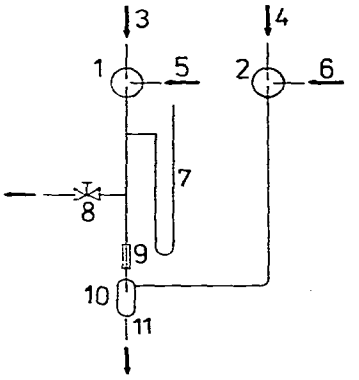


Fig. 4. Arrangement of apparatus for the preparation of mixtures with two standards of substantially different concentrations. 1–5 = Inlets; 6–8 = outlets; 9, 10, 15, 16 = diluters; 11, 14 = needle valves; 12, 13 = capillaries; 17, 18 = manometers.

Fig. 5. Arrangement of apparatus for the preparation of mixtures with two standards of substantially different concentrations, providing for varying the higher concentration of one standard over a range while keeping the lower concentration of the other standard constant. 1, 2, 10 = Diluters; 3–6 = inlets; 11 = outlet; 7 = manometer; 8 = needle valve; 9 = capillary.

CALCULATION OF CONCENTRATIONS OF STANDARD SUBSTANCES IN THE MIXTURE

The method is based on directly diluting a stream of saturated gaseous mixture with a stream of pure gas. Considering the preparation of mixtures with one standard (*cf.*, Figs. 1 and 3), the contents of the standard in the final mixture are calculated by

$$c_{i1} = \frac{P_i^0 M_i}{RT} \cdot \frac{P}{P - P_i^0} \cdot \frac{F_s}{F_s + F_{d1}} \cdot \frac{RT}{Pv} \tag{1}$$

$$c_{i2} = c_{i1} \cdot \frac{F_c}{F_c' + F_{d2}} \tag{2}$$

where c_{i1} and c_{i2} are the concentrations (mass in volume) of standard i at the outlet of the diluter of the saturated stream and at the outlet of the diluter after the capillary splitter, P_i^0, M_i, R, T, P and v are the saturation vapour pressure of the standard, molar mass of the standard, universal gas constant, absolute temperature of the saturator (thermostating bath), absolute pressure at the outlet of the saturator and the true molar volume of the saturated gaseous mixture, respectively, F_s and F_{d1} are the volumetric flow-rates of pure gas at the inlets of the saturator and of the first

diluter (item 17 in Fig. 1), respectively, F_c and F_c' are the volumetric flow-rates of the gaseous mixture and of the diluting gas alone in the mixture at the outlet of the splitting capillary (item 14 in Fig. 1), respectively, and F_{d2} is the volumetric flow-rate of pure gas at the inlet of the second diluter (item 18 in Fig. 1). The individual terms in eqn. 1 have the following meanings: $P_i^0 M_i/RT$ is the mass of component i (standard) in unit volume of the saturated gas mixture, provided the latter behaves ideally; $P/(P - P_i^0)$ is a factor representing the increase in the flow-rate in the saturator due to the generation of the vapour of substance i; $F_s/(F_s + F_{d1})$ is the dilution ratio; and RT/Pv is the correction for the non-ideality of the saturated gas mixture. Similar equations can be derived for the other modifications of the apparatus and/or for the case when two or more saturators are used.

RESULTS AND DISCUSSION

The functioning of the instrument was checked by comparing results of the chromatographic analysis of mixtures prepared as described above with the corresponding values calculated by means of eqns. 1 and 2. Benzene was employed as a model substance. All of the volumetric flow-rates were corrected so as to allow for the differences in the pressure and temperature of the gas during the calibration of the flow meters and during the checking experiments. The saturator was packed with Chromosorb P impregnated with about 30% (w/w) of benzene. The analyses were carried out by determining the absolute mass of benzene in a given (injected) volume of the mixture by direct calibration of the gas chromatograph with defined solutions of benzene in toluene. The solutions were prepared by weighing appropriate amounts of benzene in 10-ml measuring flasks and making the volume up to 10 ml with toluene. Calibration solutions with very low concentrations of benzene were prepared from the above solutions by dilution with toluene. The solutions were introduced into the gas chromatograph (Model 402; Hewlett-Packard, Avondale, Pa., U.S.A.) with a 1-μl Hamilton syringe (Micromesure, The Hague, The Netherlands). Samples of the mixture being analysed were injected with a 1-ml tuberculene syringe (Labora, Brno, Czechoslovakia). The results are summarized in Table I.

TABLE I

COMPARISON OF CALCULATED AND MEASURED CONCENTRATIONS OF BENZENE

Benzene concentration (p.p.m.)		*Difference* Δ *(%)*	*No. of determinations, n*	$\Sigma\lvert\Delta\rvert/n$
Calculated	*Measured*			
623.4	626.0	−0.42	6	0.85
581.0	583.4	−0.40		
506.6	515.4	−1.68		
342.1	337.8	+1.26		
222.5	220.8	+0.75		
114.2	114.9	−0.62		
10.10	9.91	+1.88	5	2.16
4.96	5.04	−1.61		
1.97	1.93	+2.03		
0.762	0.747	+1.97		
0.361	0.373	−3.32		

At concentrations in the range 100–600 ppm the average relative error did not exceed 1%; in the range 0.3–1 ppm the error increased to about 2%. Hence it follows that at concentrations of a few parts per billion (10^9), where it is impossible to check the contents of the standard by direct analysis of the gaseous mixture, an error of about 4% can be expected. This estimate was confirmed indirectly by measuring adsorption isotherms at that concentration level.

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