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powerful in estimating the number of component dyes and their possible spectral density distributions from those of their mixtures.

ACKNOWLEDGMENT

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Gaseous Standard Solutions of Sulfur Dioxide

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Gaseous standard solutions (GSS), i.e., gaseous mixtures of an inert gas (major component) and a gaseous reagent (minor or trace component), are prepared directly before use with the saturation method, passing the inert gas through a suitable liquid solution (mother solution). Composition of GSS is independent of gas flow rate. The GSS thus obtained is passed through the solution under study, leaving in it the gaseous reagent. Progress is reported on development of GSS's and of apparatus and procedures for using them as substitutes for liquid standard solutions (LSS). Advantages of GSS's over LSS's are discussed, as well as peculiarities of GSS's (i.e., influence of pressure and temperature, effect of GSS water content). Sulfur dioxide solutions have been made in the GSS concentration range 6×10^{-7} – $1.2 \times 10^{-3}M$ (15–30,000 ppm v/v) with a relative standard deviation of 0.1–0.3% (1–2% at $10^{-7}M$ level) and a comparable accuracy. The apparatus is ready for use at any moment, even after a long non-use period of time. Mother solutions are very stable and contain a high reserve of gaseous reagent.

TITRIMETRIC ANALYSIS is founded on the use of standard solutions, i.e., liquid solutions of a reagent in a suitable solvent at accurately known and stable concentration.

Though a large number of liquid standard solutions (LSS) are in use, several analytical possibilities are precluded by some limitations in preparing and using LSS's. Gaseous reagents with low solubility in the solvent cannot be used, because of continuous loss of the reagents, due to the dependence of their solubility on their partial pressure in the gaseous phase above solution. Some reagents are unstable with respect to oxygen and carbon dioxide and their LSS's should be protected from air during preparation, storage, and use. When very small quantities of reagent are involved, difficulties arise. In these cases small volumes or/and high dilutions should be used. The delivery of very small volumes is now possible, but high dilutions are, on the contrary, not reliable because of loss of reagent by adsorption on the walls of the vessels and by reaction with trace amounts of gaseous, liquid, and solid impurities and because of the presence in the solution of solvent impurities and of impurities desorbed from the walls of the vessels, which could interfere in the system under study by competition with the reagent. Finally, the use of LSS's implies in every case the adding to the system under study of some solvent and an undesired and sometimes annoying dilution.

We maintain that these difficulties can be surmounted, when gaseous reagents are involved, with the use of gaseous standard solutions (GSS). We maintain also that GSS's could

be advantageously employed: in substitution for many LSS's in acid-base, redox and precipitation reactions and titrations, in aqueous as well as in nonaqueous media; as standards in trace gas analysis and in stack gas analysis; and as standards for analytical methods and detectors. For these purposes we are developing a number of GSS's and apparatus and procedures to prepare and to use them.

A GSS is defined as a gaseous mixture of an inert gas (major component) and a gaseous reagent (minor or trace component). We prepare GSS's, directly before use, with the saturation method, passing the inert gas through a suitable liquid aqueous solution (mother solution). During the passage, which can be performed with a wide range of flow rate, the inert gas becomes saturated with the gaseous reagent. The GSS thus obtained passes through the solution in study leaving in it the gaseous reagent. The volume of the inert carrier gas is finally measured, from which the amount of gaseous reagent employed is obtained.

We have already commented on hydrochloric acid GSS's (HCl-GSS), in the concentration range 1.2×10^{-6} – $1.8 \times 10^{-3}M$ (30–45,000 ppm v/v), and on ammonia GSS's (NH₃-GSS), in the concentration range 1.5×10^{-6} – $2 \times 10^{-3}M$ (360–50,000 ppm v/v) (1).

In the present paper we discuss sulfur dioxide GSS's (SO₂-GSS), prepared in the concentration range 6×10^{-7} – $1.2 \times 10^{-3}M$ (15–30,000 ppm v/v) from aqueous pH-buffered mother solutions; a new apparatus and procedure for generating and using GSS's, which constitute an improvement on those previously described (1, 2); the influence of atmospheric pressure and room temperature variations on reliability, precision and accuracy; the variation of the GSS concentration with consumption of the gaseous reagent and the means to minimize this inconvenience; and the effect of the GSS water content.

EXPERIMENTAL

Mother solutions were prepared in 200-ml stocks by adding known volumes of a 3M citric acid solution to a sodium sulfite solution. The sodium sulfite content was fixed at 0.12 mole/200 ml and that of citric acid ranged from 0.03 to 0.24 mole/200 ml.

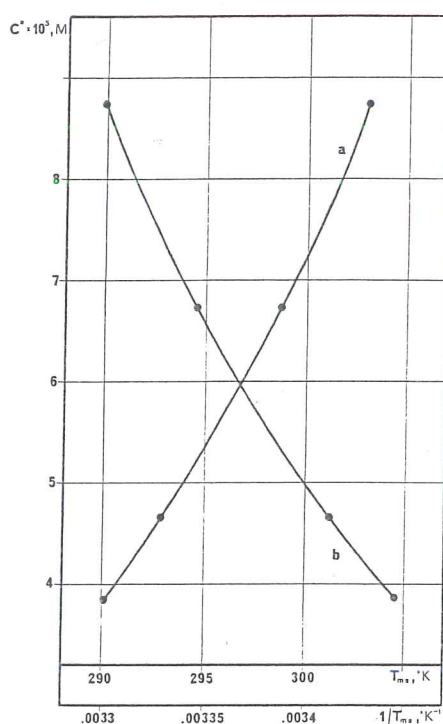
The concentration of the SO₂-GSS's was determined by means of visual titrations with 1–10 ml portions of freshly

(1) E. Scarano, M. Forina, and G. Gay, *ANAL. CHEM.*, **43**, 1310 (1971).

(2) E. Scarano, G. Gay, and M. Forina, *ibid.*, p 206.

Table I. Results of Titrations with SO₂-GSS's $T_{ms} = 293\text{ }^{\circ}\text{K}$; $T_r = 296-8\text{ }^{\circ}\text{K}$

Mother solution		Series of titrations	I_2 , μeq	V_{N_2} , ml	C^* (M)	Rel std dev, %
Citric acid (mole)	pH at 293 $^{\circ}\text{K}$					
0.240	2.62	1	100	41.0	1.219×10^{-3}	0.1
		2	80	32.8	1.219×10^{-3}	0.3
0.150	3.09	3	40	43.1	4.64×10^{-4}	0.1
		4	32	34.5	4.64×10^{-4}	0.0
0.075	4.09	5	4.0	42.2	4.74×10^{-5}	0.1
		6	3.2	33.9	4.72×10^{-5}	0.3
		7 ^a	5.0	28.6	8.74×10^{-5}	0.3
0.075	4.09	8	4.0	42.7	4.68×10^{-5}	0.2
		9 ^b	4.0	42.7	4.68×10^{-5}	0.3
0.045	5.13	10	0.50	53.3	4.69×10^{-6}	0.4
		11	0.40	42.7	4.68×10^{-6}	0.4
0.030	5.98	12	0.80	646	6.19×10^{-7}	1.6
		13	0.60	495	6.06×10^{-7}	2.2

^a $T_{ms} = 303\text{ }^{\circ}\text{K}$.^b After 72 hours.Figure 4. Effect of mother solution temperature on C (a) C^* vs. T_{ms} ; (b) C^* vs. $1/T_{ms}$

The passage of 2 l. of nitrogen through 10 ml of a $10^{-2}N$ iodine solution, followed by titration with thiosulfate, showed a loss of iodine lower than 1%, which corresponded to a maximum error of 0.05% for a titration in our experimental conditions. A trap containing 1 ml of a solution with 0.06 μeq of iodine and some starch, put downstream and connected with glass tubing to the B cell, showed that the sulfur dioxide was thoroughly absorbed in the B cell during a titration. The same conclusion was achieved by back-titration with thiosulfate of excess iodine in the B cell, after the passage of an amount of SO₂-GSS in defect.

RESULTS

Some representative results are summarized in Table I. Each series of titrations consisted in 4–20 titrations performed

Table II. Effect of Temperature on Concentration of SO₂

T_{ms} , $^{\circ}\text{K}$	C^* (M)
290.1	3.85×10^{-5}
293.0	4.63×10^{-5}
298.7	6.67×10^{-5}
303.0	8.74×10^{-5}

in the same experimental conditions. Some series of titrations were performed with the same 200-ml stock of the mother solution (series 1-2, 3-4, 5-6-7, 8-9, 10-11, 12-13, in Table I). Precision was expressed as relative standard deviation (rel std dev); higher values of relative standard deviation at the $10^{-7}M$ level were attributed to difficulty in performing titrations with very small quantities of iodine. Accuracy was determined with different amounts of iodine. Precision and accuracy in preparing mother solutions were as high as titrations (compare series 5 and 8 in Table I).

The composition of the SO₂-GSS's were unaffected by long non-use periods of time (compare series 8 and 9 in Table I).

The SO₂-GSS concentration as a function of composition and pH of the mother solution is reported in Figure 3.

The effect of the mother solution temperature on the concentration of SO₂-GSS is reported in Figure 4, drawn from the experimental data given in Table II.

In the neighborhood of 293 $^{\circ}\text{K}$, the dependence was 6%/degree. In view of the rather high temperature coefficient for the SO₂-GSS preparation, the temperature should be well-controlled. Not much trouble was encountered in this respect, certainly because of the high thermostating ability of the temperature control system employed.

The time required for a titration to be performed, with a mean gas flow rate of 1 ml/sec, ranged from 4 to 15 min (corresponding to a SO₂-GSS volume from 50 to 500 ml), including 2–3 min for emptying, washing, and filling the B cell.

Some anomalous results were obtained in preliminary experiments when the SO₂-GSS concentration was lower than $10^{-5}M$. The lower the concentration, the higher the anomaly. After prolonged periods of non-use, the SO₂-GSS concentration resulted in values higher or lower than the expected value. Repeated titrations showed a drift toward the stable expected value of the concentration in both cases.

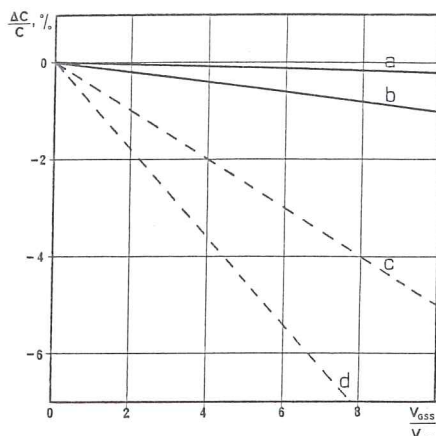


Figure 5. Lowering of C with consumption of SO_2 -GSS. Per cent lowering of C vs. $V_{\text{GSS}}/V_{\text{ms}}$ [total delivered volume of SO_2 -GSS (ml)/volume of the mother solution (ml)]

(a) buffered mother solution, $C = 10^{-5}M$ (experimental and calculated) (b) buffered mother solution, $C = 10^{-4}M$ (experimental and calculated); (c) Unbuffered mother solution, $C = 10^{-5}M$ [calculated for a mother solution containing 0.8 g/l. of Na_2SO_3 , and 0.004M in H_2SO_4 (11)]; (d) unbuffered mother solution, $C = 10^{-4}M$ [calculated for a mother solution containing 3.3 g/l. of Na_2SO_3 , and 0.017M in H_2SO_4 (11)]

Lower values were connected with exposure of the B cell to the air, and higher values were obtained when the B cell was left filled with a dilute aqueous sulfur dioxide solution. It seemed probable that the phenomenon was related to oxidants or reductants accumulated on the walls of the B cell and particularly on or in plastic material (silicone rubber) used to close the tip of the buret. The trouble could be eliminated by leaving the B cell filled with a dilute sulfur dioxide solution and washing it with an iodine solution before a set of titrations.

Calculation of the Concentration of the GSS's. The concentration of the GSS's, C (M) is calculated exactly by means of previously reported equations (1), which take into account the nitrogen (inert gas) volume read in the gas buret, V_{N_2} (ml), the mother solution temperature, T_{ms} (°K), the room temperature, T_r (°K), the atmospheric pressure, P , the overpressure in the A cell, ΔP , the water partial pressure in the gas buret, $P_{\text{H}_2\text{O}}$, the water partial pressure in the A cell, $P_{\text{H}_2\text{O}}^A$, the gaseous reagent partial pressure, P_{gr} (all pressures in mm Hg).

C is useful in studies of equilibria in the liquid phase through the composition of the equilibrium gaseous phase (2, 7).

For analytical purposes, i.e., for standardizations and titrations, the following simplified equation can be used:

$$C^* = \text{mmole}/V_{\text{N}_2} = \text{meq}/2 V_{\text{N}_2} \quad (1)$$

where mmole = millimoles of the gaseous reagent, and meq = milliequivalents of iodine. Provided that T_r and P are nearly constant during titrations, C^* gives good results, no matter how much it differs from C (1).

For more accurate calculations, or when results obtained at fairly different T_r and P values have to be matched, their

(7) R. A. Robinson and Roger G. Bates, *ANAL. CHEM.*, **43**, 969 (1971).

Table III. Validity of Equations 5 and 6 Proved by Calculation

T_r , °K	P , mm Hg	$C^*(M)^a$	$(C^*)_{293}(M)^b$
288	740	1.0174×10^{-4}	0.9922×10^{-4}
288	780	1.0174×10^{-4}	0.9922×10^{-4}
293	760	0.9937×10^{-4}	0.9937×10^{-4}
298	740	0.9683×10^{-4}	0.9917×10^{-4}
298	780	0.9691×10^{-4}	0.9925×10^{-4}

^a Calculated from Equation 2. $C = 10^{-4}M$; $T_{\text{ms}} = 293$ °K; P variable; $P_{\text{H}_2\text{O}} = 17.5$ mm Hg (8); $\Delta P = 6.2$ mm Hg; $P_{\text{H}_2\text{O}}^A = 17$ mm Hg (a logical compromise among water vapor pressure values at 293 °K of pure water (17.5 mm Hg), a saturated sodium sulfite solution (16.5 mm Hg) (9) and a saturated sodium tartrate solution (16 mm Hg) (10); $P_{\text{gr}} = CRT_{\text{mr}}(1)$.

^b Calculated from Equation 6.

influence on C^* must be taken into account. The influence of P is very low (a P variation from 740 to 780 mm Hg gives an error $\leq 0.1\%$), but the effect of T_r is not negligible. An equation, taking into account the T_r influence, can be obtained for $(C^*)_{\text{R}}$, i.e., the value of C^* at a reference temperature $(T_r)_{\text{R}}$ and a reference pressure $(P)_{\text{R}}$, valid for given T_r and P intervals.

From the exact equation for C^* (1):

$$C^* = C \frac{T_{\text{ms}}}{T_r} \frac{(P - P_{\text{H}_2\text{O}})}{P + \Delta P - P_{\text{H}_2\text{O}}^A - P_{\text{gr}}} \quad (2)$$

by differentiation (C , T_{ms} , P , ΔP , $P_{\text{H}_2\text{O}}^A$, P_{gr} are T_r independent) we obtain:

$$dC^* = -C^* \frac{dT_r}{T_r} - C^* \frac{dP_{\text{H}_2\text{O}}}{P - P_{\text{H}_2\text{O}}} \quad (3)$$

Provided that $[T_r - (T_r)_{\text{R}}]$ is sufficiently small:

$$\Delta C^* = C^* \left(-\frac{T_r - (T_r)_{\text{R}}}{T_r} - \frac{\Delta P_{\text{H}_2\text{O}}}{P - P_{\text{H}_2\text{O}}} \right) \quad (4)$$

and the final equation is obtained:

$$(C^*)_{\text{R}} = (C^* - \Delta C^*) = C^* \left(2 - \frac{(T_r)_{\text{R}}}{T_r} + \frac{\Delta P_{\text{H}_2\text{O}}}{P - P_{\text{H}_2\text{O}}} \right) \quad (5)$$

If $(T_r)_{\text{R}} = 293$ °K, $(P)_{\text{R}} = 760$ mm Hg, the T_r range = 288–298 °K, and the P range 740–780 mm Hg, we have $\Delta P_{\text{H}_2\text{O}} = 1.1 [T_r - (T_r)_{\text{R}}]$ mm Hg (8); $(P - P_{\text{H}_2\text{O}}) = 742$ mm Hg [for P and $P_{\text{H}_2\text{O}}$ we take the middle values in the T_r and P chosen ranges (8)]; and

$$(C^*)_{293} = C^* \left[2 - \frac{293}{T_r} + 0.00148 (T_r - 293) \right] \quad (6)$$

The validity of Equations 5 and 6 has been proved by calculation. See Table III.

Consumption of Gaseous Reagent and Composition of GSS. The composition of a GSS is obviously affected by the consumption of the gaseous reagent in the mother solution. The lowering of C with the use makes it necessary to repeat calibration of the GSS every suitable, rather large, number of titrations (1). Although calibration is a simple matter, this nuisance can be minimized with a relatively large volume of the mother solution (1), with two stocks of the mother solution

(8) "Handbook of Chemistry and Physics", 49th Edition, The Chemical Rubber Company, Cleveland, Ohio, 1969, p D-109.

(9) *Ibid.*, p E-37.

(10) H. H. Lowry and S. O. Morgan, *J. Amer. Chem. Soc.*, **46**, 2192 (1924).

put in series (11), with a buffered mother solution, or finally with a combination of these devices.

In this paper we refer to the possibility offered by the use of pH-buffered mother solutions, in the case of an acidic gaseous reagent HB, like H_2SO_3 .

The value of C is related to the concentration of HB in the mother solution, C_{HB} (1, 2):

$$C = KC_{\text{HB}} \quad (7)$$

A high reserve of HB is in turn dependent on a high value of C_{B^-} , i.e., the concentration of B^- , the conjugate base of HB. Provided that $C_{\text{HB}}/C_{\text{B}^-}$ will be low in any case, we can obtain both a high reserve of HB and a predetermined value of C (between certain limits), pH being the determining factor:

$$C_{\text{HB}}/C_{\text{B}^-} = K_{\text{HB}}/C_{\text{H}^+} \quad (8)$$

where K_{HB} is the acid constant of HB and C_{H^+} the hydrogen ion concentration.

After the choice of C has been made and the approximate value of pH calculated by means of Equations 7 and 8, a convenient pH buffer must be chosen from the literature.

The effectiveness of this way to limit the drift of C with consumption, in the case of SO_2 -GSS and citric acid-citrate buffer, is shown in Figure 5. Of course the limitation of the drift will be more and more satisfying with two stocks of buffered mother solution put in series.

The validity of Equations 7 and 8, in the case of SO_2 -GSS's, is shown by the data in Table IV.

Effect of GSS Water Content. The water content of a GSS, together with the solubility of its gaseous reagent in water, can seriously affect the precision and accuracy of results.

If both water content and solubility are high, the worst situation arises. The water vapor easily condenses on the tubing walls, the liquid water so obtained in turn dissolves the gaseous reagent, and the composition of the GSS is subject to irregular diminutions. This situation is encountered, e.g., with HCl-GSS's produced from relatively dilute aqueous hydrochloric acid mother solutions ($<10M$) (2). To obtain stable HCl-GSS's, aqueous mother solutions of dilute hydrochloric acid-concentrated lithium chloride (2), or of dilute hydrochloric acid-concentrated sulfuric acid (1) may be used, because these solutions possess very low water activities. Troubles with HCl-GSS's mainly arise from the very high solubility of hydrochloric acid in water. With NH_3 -GSS's, difficulties are smaller, because of the low solubility of ammonia in water at low ammonia partial pressure. Therefore, the very low solubility of sulfur dioxide in water makes the preparation and use of SO_2 -GSS's a more simple matter.

A simple trick for minimizing troubles seems to be that of keeping the mother solution temperature below the room temperature. In the case of NH_3 -GSS's (unpublished experiments), good results were obtained making use of that trick. In the case of SO_2 -GSS's, good results were obtained with and without it.

Summarizing, when the solubility in water of the gaseous reagent is low, high water content in both mother solution and GSS are permissible. When, on the contrary, the solubility is high, mother solutions with low water partial pressure must be looked for. The above arguments are supported by data in Table V.

Table IV. Data Showing Validity of Equations 7 and 8

pH (measured)	$C_{\text{H}_2\text{SO}_3}(M)$	$C^*(M)$	$K = C^*/C_{\text{H}_2\text{SO}_3}$
2.62	8.09×10^{-2}	1.22×10^{-3}	0.0151
3.09	3.01×10^{-2}	4.64×10^{-4}	0.0154
4.09	3.15×10^{-3}	4.70×10^{-5}	0.0149
5.13	2.85×10^{-4}	4.68×10^{-6}	0.0164
5.98	3.72×10^{-5}	6.12×10^{-7}	0.0165

where $C_{\text{H}_2\text{SO}_3} = 0.6/(1 + K_1/C_{\text{H}^+} + K_1K_2/C_{\text{H}^+}^2)$; 0.6 = total sulfite concentration = $C_{\text{Na}_2\text{SO}_3}$; K_1 and K_2 are the activity acid constants of H_2SO_3 and HSO_3^- , respectively, 1.54×10^{-2} and 1.02×10^{-7} .

Table V. Solubility of Some Gaseous Reagents in Water at 20°C

Gaseous reagent	Solubility (M)		
	$P_{\text{gr}} = 760$ mm Hg	$P_{\text{gr}} = 1$ mm Hg	v (ml) ^a
HCl	19.4 ^b	7.4 ^b	135
NH ₃	31.3 ^c	0.1 ^d	1.7
SO ₂	1.74 ^b	7×10^{-3e}	0.1
H ₂ S	0.116 ^b	1.5×10^{-4f}	0.003

^a v = volume of a $5.5 \times 10^{-5}M$ GSS ($P_{\text{gr}} = 1$ mm Hg) containing the amount of gaseous reagent necessary to saturate 1 μl of water, under $P_{\text{gr}} = 1$ mm Hg.

^b Calculated from solubility data in "International Critical Tables," McGraw-Hill, New York, N.Y., 1928, Vol. III, p 301.

^c Calculated from solubility data in N. A. Lange, "Handbook of Chemistry," McGraw-Hill, New York, N.Y., 1967, p 1099.

^d Calculated from our experimental data (1).

^e Calculated from our experimental data (this paper).

^f Calculated from solubility data, N. A. Lange, "Handbook of Chemistry," McGraw-Hill, New York, N.Y., 1967, p 1101.

DISCUSSION

Gas mixtures of a gaseous reagent and an inert gas have been prepared, in the field of analytical chemistry, as standards for trace gas analysis (11-15) and as GSS's in substitution for LSS's (1).

Several methods of preparation have been indicated (12-14), but only three of these methods seem to us to be reliable, i.e., the electrolytic method, the permeation tube method, and the saturation method.

The first method (13) consists in the enrichment of the flowing inert gas with the electrolytically generated reagent. The second method (14, 15) comprises the immersion in the flowing inert gas of an inert plastic tube within which is sealed, in liquid state, the gaseous reagent. Permeation of the gaseous reagent through the walls of the tube occurs at a constant rate, at a given temperature, for a long time. The composition of the resulting mixture is fixed by the flow rate of the inert gas. With the saturation method (1, 11, 12), the inert gas is allowed to pass through a suitable liquid solution, the mother solution (1), where the gaseous reagent is dissolved. In this passage it becomes saturated by volatile components of the mother solution, i.e., the gaseous reagent and the solvent (water).

The electrolytic method has been indicated for the preparation of gaseous standards of the following chemical species:

- (12) B. E. Saltzman, *ANAL. CHEM.*, **33**, 1100 (1961).
- (13) P. Hersch, C. J. Sambucetti, and R. Deuringer, *Chim. Anal.*, **46**, 31 (1964).
- (14) E. O'Keeffe and G. C. Ortman, *ANAL. CHEM.*, **38**, 760 (1966).
- (15) F. P. Scaringelli, S. A. Frey, and E. Saltzman, *Amer. Ind. Hyg. Ass. J.*, **28**, 260 (1967).

(11) E. Erdős and J. Bareš, *Collect. Czech. Chem. Commun.*, **29**, 2718 (1964).

oxygen, hydrogen, deuterium, nitrogen, chlorine, carbon dioxide, nitrogen oxide, ethylene, ozone, arsine, stibine (13).

With the permeation tube method, sulfur dioxide, nitrogen dioxide, propane, and butane standards have been successfully prepared in ppm and in ppb concentration ranges (14, 15).

The saturation method has been used to prepare gaseous solutions of bromine, hydrogen chloride, hydrogen cyanide, monoethanolamine, at relatively high concentration level (12); sulfur dioxide in the concentration range 1.2×10^{-5} – 1.5×10^{-4} M (11) (the carrier gas used was nitrogen, which passed through two 2-l. thermostated glass bottles put in series, containing sulfuric acid added with some sodium sulfite); hydrochloric acid and ammonia (1).

There are three major differences among these methods. The first difference is related to the reserve of the gaseous reagent. The reserve is very high with the permeation tube method: the composition of the gas mixture is not influenced by the consumption of the gaseous reagent, until the enclosed liquified gas is nearly exhausted, *i.e.*, after months (14, 15). With the electrolytic enrichment, the reserve should also be high (13). The question as to how to make the reserve high with the saturation method has been previously discussed in this paper.

The second difference lays on the relation between the composition of the gas mixture and the inert gas flow rate. With the saturation method, the composition is independent of the gas flow rate. The method permits both a wide range of gas flow rate and the delivery of very small volumes of GSS (and of very small quantities of gaseous reagent) at will and easily (1, 2). On the contrary, with the other two methods,

the composition is strongly dependent on the gas flow rate and accurate gas flow rate measurement and maintenance are necessary (with the electrolytic method accurate electric current measurement and maintenance are also necessary). Variation of the composition of the gas mixture is obtained changing the composition of the mother solution, with the saturation method. More simply, with the permeation tube method, changing the gas flow rate (with the electrolytic method, also changing the electric current); but, especially with high values of gas flow rate (and low values of electric current) difficulties and errors arise (13).

The third difference arises from the time necessary to obtain a constant composition of the gaseous mixture, following a non-use period of the apparatus. With the saturation method the composition is unaffected by every sort of non-use period (1, 2). With the other two methods, a certain time, although short, is necessary to reach steady conditions between the inert gas flow rate and the gaseous reagent generation rate. Moreover, any interruption of the gaseous flow, or variation of its rate (and of the electric current) is a source of troubles and errors.

The comparison of the performance differences among the three methods is favorable to the saturation method for its simplicity, independence of gas flow rate, and immediate availability at any time.

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NOTES

Identification of Flame Retardant Textile Finishes by Pyrolysis–Gas Chromatography

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THE STUDY OF FLAME RETARDANT chemicals currently constitutes a very active area of textile research. A wide variety of reagents has been demonstrated to reduce fabric flammability. Many, if not most, of the more successful of these are phosphorus-containing compounds (1).

¹ Present address, Phillips Fibers Technical Center, Greenville, S.C.

This note presents a rapid and straightforward technique for the identification of selected examples of these phosphorus derivatives on fabric.

EXPERIMENTAL

All analyses were performed on a Tracor MicroTek 220 vapor phase chromatograph equipped with the flame photometric detection system developed by Brody and Chaney (2)

(1) John W. Lyons, "The Chemistry and Uses of Fire Retardants," John Wiley and Sons, New York, N. Y., 1970, pp 29–74.

(2) Sam F. Brody and John E. Chaney, *J. Gas Chromatogr.*, **4**, (2) 42 (1966).