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QUANTITATIVE DETERMINATION OF SULFUR COMPOUNDS IN THE GAS PHASE OF CIGARETTE SMOKE

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SUMMARY

Flame photometric detection gas chromatography affords a reliable approach for the determination of sulfur compounds in smokes. Reliable quantitative data can only be generated if the analytical system allows a minimum of time to elapse between smoke generation and the onset of analyses. Contact with stainless-steel surfaces must be minimized and the chromatographic column must be conditioned to avoid irreversible adsorption. Typical cigarettes deliver approximately 85 μg of H_2S, 35 μg of COS, 2 μg of CS_2, and 3 μg of SO_2 when smoked under standard conditions. The gas phases of smokes contain at least 28 sulfur components. Quantitative distribution of these components is highly sensitive to sampling methodologies.

INTRODUCTION

Applications of flame photometric detection gas chromatography (GC) to the study of sulfur components in the gas phase of cigarette smoke have suggested that this component of smoke is significantly more complicated than had been assumed. Groenen and Van Gemert[1] found up to 37 sulfur-containing species in the gas phases of various cigarette smokes. Guerin[2] reported the presence of at least eleven sulfur-containing components and found that previously held estimates of the relative quantities of H_2S, COS, and SO_2 appeared to be in error. Absolute quantitative deliveries of the sulfur gases and organosulfur components were not reported in either work. Quantitative studies, while demonstrating the potential utility of the method, enjoyed only limited success.

A system is described here which allows the generation of reliable quantitative results for sulfur constituents of cigarette smokes. Results are reported for the H_2S, COS, SO_2, and CS_2 deliveries of typical cigarettes. Applications of the system for a further study of the sulfur components of smokes are discussed briefly.

EXPERIMENTAL

A Model MT 220 gas chromatograph (Tracor, Austin, Texas, U.S.A.) equipped with a flame photometric detector (FPD) and a 6 ft. × 1/8 in. O.D. fluoroelastomer (FEP) column packed with Tracor Special Silica was used for the determination of COS, H_2S, CS_2, and SO_2. The column was operated at room temperature (24 °C) with a nitrogen carrier gas flow-rate of 15 ml/min. Inlet and detector temperatures were 75 °C and 125 °C, respectively. An 18 ft. × 1/4 in. O.D. glass column of 20% FFAP (Varian, Walnut Creek, Calif., U.S.A.) on 60–80 mesh Chromosorb W AW-DMCS was used for surveys of higher-boiling sulfur components. Chromatographic conditions were as follows: column program, isothermal at 24 °C for 6 min then 4 °C/min to 225 °C; nitrogen carrier gas flow-rate, 60 ml/min; inlet and detector temperatures, 225 °C. A sample volume of 0.14 ml of gas phase was injected for the determination of the low-boiling sulfur components and a volume of 3.5 ml was injected for high-boiling components. For both columns, FPD gases were: hydrogen 180 ml/min, air 40 ml/min, and oxygen 20 ml/min.

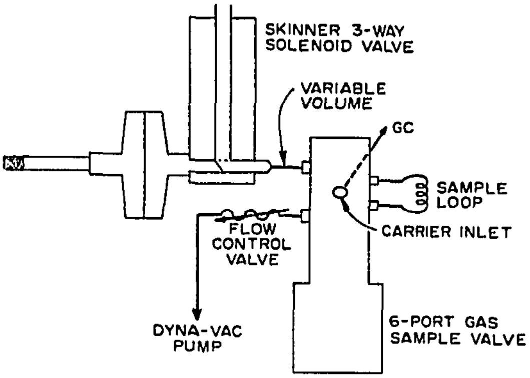


Fig. 1. Single-port smoking machine.

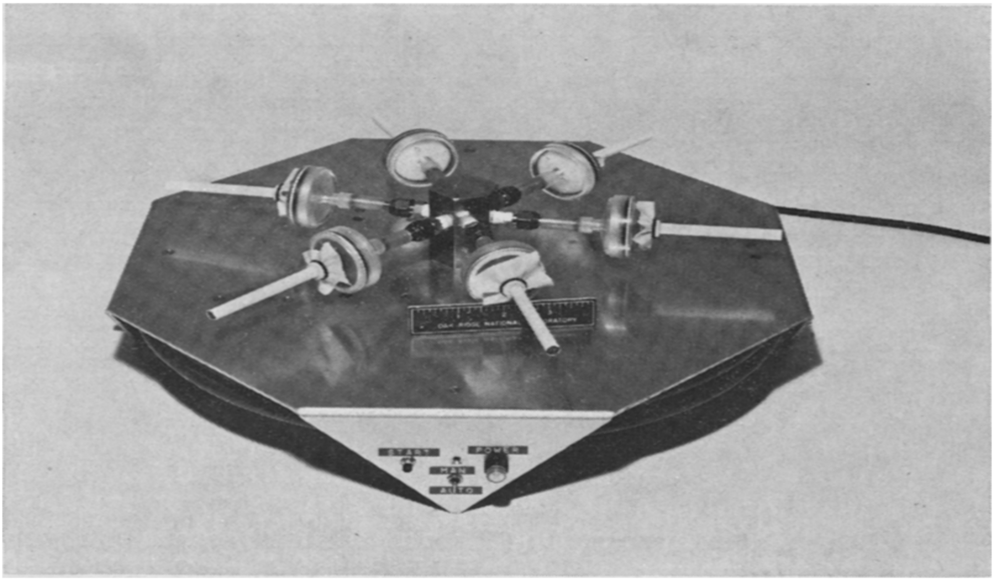


Fig. 2. Six-port smoking machine-"Hexapuffer".

Two smoke generation-sampling systems were used in this work. A single-port machine (Fig. 1), consisting of a filter assembly, a Skinner solenoid valve, a Varian 6-port gas sampling valve, a Dyna-vac vacuum pump, and an electromechanical cam timer necessary to achieve standard puff parameters, was used for preliminary quantitative studies. All cigarettes smoked on the single-port machine were conditioned and weight-selected as follows: Cigarettes were conditioned at 60 ± 2% RH and 75 ± 2 °F. Cigarettes that were free from obvious defects, *e.g.* pin holes, frayed wrappers and/or loss of filler, were weight-selected from a batch of 100–200 cigarettes by discarding those differing by more than ±20 mg from the average and setting aside as samples those within ±20 mg of the average weight of the batch. Resistance-to-draw (*RTD*) of the weight-selected cigarettes was determined and only those that matched within ±5% of the average *RTD* were used.

A modified version of the six-port puff averaging system developed by Norman *et al.*[3] (Fig. 2) was used for generating the quantitative data reported here. Modifications include the use of Teflon flow lines, direct vacuum puffing rather than evacuated manifold puffing, and the incorporation of manual operation to allow smoking cigarettes of large puff number. A detailed description of the system is in preparation.

All cigarettes smoked on the Hexapuffer were conditioned for at least 48 h at 60% RH and 75 °F before smoking. Cigarettes were randomly selected from experimental products on hand or single packs of commercial products purchased locally. Cigarettes were inserted through a latex dental dam attached to standard Cambridge filter assemblies[4] and lit using an electric cigar lighter.

Standards of carbonyl sulfide and of hydrogen sulfide, both approximately 500 ppm in nitrogen, were prepared by Matheson Gas Products (East Rutherford, N.J., U.S.A.). Standard sulfur dioxide, approximately 700 ppm in nitrogen, was prepared locally and standardized iodometrically. Carbon disulfide standards were prepared in *n*-hexane using reagent-grade chemicals. Sulfur compounds used for co-chromatographic identification of peaks were obtained primarily from Polyscience Corporation (Kit No. 71B). Gaseous standards for quantitative calibration were introduced either as received or by dynamic dilution with nitrogen.

RESULTS AND DISCUSSION

Flame photometric detection provides a convenient method for visualizing sulfur-containing components in smokes. The sensitivity is such as to allow detecting trace components and selectivity is such as to allow detecting sulfur components in the presence of great excesses of other smoke constituents. Determination of the absolute quantities of these compounds delivered in smokes is complicated by their generally high reactivity. The problem is particularly severe for hydrogen sulfide and for sulfur dioxide.

Table I illustrates the loss of hydrogen sulfide resulting from the use of stainless-steel tubing in the smoking machine and in the transfer line. Considering a total residence time of no more than 4 sec and that the sample is swept to the instrument in a stream of inert gas, the extent of the loss, 60–70%, is surprisingly high. Losses as a result of stainless-steel tubing are apparently due to a process

TABLE I

EFFECT OF STAINLESS STEEL ON HYDROGEN SULFIDE DELIVERIES

Product	H_2S (*μg/cigarette*)*		*Per cent loss*
	Stainless-steel tubing	*Teflon tubing*	
Kentucky Reference-1 R1	27	90	70
Commercial, 85-mm non filtered	32	79	59
Commercial, 85-mm charcoal filter	7	27	74

* Single-port smoking device

TABLE II

EFFECT OF CONSTRUCTION MATERIALS AND AGING ON THE GAS PHASE SULFUR COMPOSITION

Peak No.	*Per cent increase* in peak height*		
	Teflon loop Age, 30 sec	*Stainless-steel loop Age, 0 sec*	*Stainless-steel loop Age, 30 sec*
1	—**	—	—
2	—	—	—
3–5	See Tables I and III		
6	—	—	—
7	—	—	—
8	—	—	100
9	—	—	—
10	50	0	50
11	0	0	300
12	0	0	—
13	50	0	50
14	0	0	200
15	50	0	50
16	50	50	200
17	10	0	50
18	—	—	—
19	—	—	—
20	—	—	—
21	—	—	—
22	60	200	300
23	50	0	70
24	10	0	200
25	50	0	50
26	40	60	220
27	40	60	300
28	10	20	200

* Increase relative to Teflon loop, age 0 sec.

** < 10% increase.

more complicated than simple reaction with or adsorption by the metal surface. Losses due to adsorption alone would tend to cancel since standard and sample are routed identically. The presence of the other gas phase constituents may accelerate losses of hydrogen sulfide. Data in Table II, illustrating a substantial increase in higher-molecular-weight sulfur components in the presence of stainless steel further suggests an involvement by other smoke constituents. The metal surfaces may both irreversibly adsorb the reactive sulfur gases and catalyze reaction with other gas phase constituents. Considering that the increase in organosulfur constituents illustrated in Table II results from replacing only the Teflon sampling loop with stainless steel and that contact times are in the order of 4 sec or less, catalysis may be a major factor.

Aging is also a major factor in changing the composition of the sulfur component of smokes. Significant increases in higher-molecular-weight sulfur compounds are observed (Table II) when the sample is held for 30 sec in a Teflon loop before injection into the chromatograph. Lower-molecular-weight components, particularly hydrogen sulfide, exhibit a simultaneous decrease in concentration (Table III). The finding that the sulfur dioxide concentration does not change is unexpected. A possible explanation is that sulfur dioxide is formed as efficiently as it is consumed. No substantive data are available for this view, however.

TABLE III

DECREASE IN SULFUR DELIVERY WITH AGING

Age 0 = 1.00.

Age (sec)	*Relative quantity*			
	COS	*H_2S*	*CS_2*	*SO_2*
10	0.93	0.75	0.98	1.00
30	0.87	0.68	0.79	1.00
60	0.65	0.31	0.75	1.00

A final difficulty associated with the generation of quantitative data concerns the GC process itself. Hydrogen sulfide and sulfur dioxide in particular, are irreversibly lost to the column packing. Chromatographic packings suggested for the analyses of sulfur gases at high concentrations inevitably fail in applications to trace quantities. Of the packings evaluated for quantitative analyses, Porapak Q was found the most adsorptive while Deactigel, Porapak P, and Tracor Special Silica were found, respectively, superior. No packing evaluated to date was found completely free of adsorptive properties. The difficulty was overcome in this work by "conditioning" the packing through repetitive injections of H_2S and, when SO_2 is to be analyzed, SO_2 at the beginning of the day. Fifteen 5-ml injections of a gas standard with the average of the last three injections measured as a calibration point are sufficient to condition the column. No further losses occur with continuous use. Fig. 3 illustrates the chromatographic response observed on injection of gas phase on to the Tracor Special Silica Column.

Table IV summarizes the sulfur delivery of typical commercial and experimental cigarettes as determined by use of the Tracor Special Silica column and the puff averaging smoking device. Using randomly selected cigarettes, *i.e.* not selected by weight or pressure drop, allows the analyses to be carried out with a coefficient of variation of approximately ±5% when three machine loads are used. Results obtained with the puff averaging system are in excellent agreement with those obtained with the single-port machine (compare Tables I and IV). As many as three determinations can be carried out without changing Cambridge filters, indicating little effect on the analysis by accumulated tar.

TABLE IV

QUANTITIES OF COS, H_2S, CS_2 AND SO_2 DELIVERED BY COMMERCIAL AND EXPERIMENTAL SMOKING PRODUCTS

Product	*Amount of sulfur compound (μg/cigarette)*			
	COS	*H_2S*	*CS_2*	*SO_2*
Kentucky Reference-1R1	41	87	1.8	2.6
Commercial, 85-mm non-filtered	30	81	1.0	3.7
Commercial, 85-mm cellulose acetate-filtered	30	89	2.0	3.3
Commercial, 85-mm charcoal*-filtered	27	25	0.6	2.9
Experimental (A), 85-mm non-filtered, control	22	55	1.2	4.0
Experimental (A), 85-mm non-filtered, low-ammonium sulfamate	24	65	2.0	6.3
Experimental (A), 85-mm non-filtered, high-ammonium sulfamate	38	102	2.6	8.8
Commercial little cigar, 85-mm filtered	37	112	1.6	7.0
Marihuana, 85-mm non-filtered	29	80	2.0	2.2

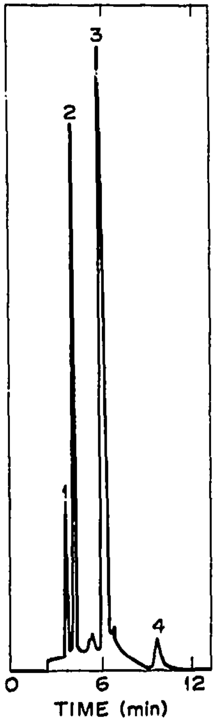
* Cellulose acetate–charcoal–cellulose acetate.

The hydrogen sulfide delivery is seen to be approximately twice that reported by Terrell and Schmeltz[5] and by Mattina[6]. Carbonyl sulfide deliveries are found to be 30 to 50% that of hydrogen sulfide rather than five to twenty times that of hydrogen sulfide as reported. Sulfur dioxide is shown to be present to the extent of a few per cent of hydrogen sulfide rather than in equal quantities. Carbon disulfide levels are in good agreement with those reported by Phillipe and Hobbs[7]. Since aging and metal surfaces should not have been serious problems in these studies, differences are likely a result of the use of non-specific analytical techniques or reactions after trapping.

As further evidence of the reliability of the method, product modifications expected to affect sulfur delivery were found to do so. Cigarettes containing ammonium sulfamate produced almost twice the H_2S and SO_2 deliveries when compared to the same blend without the additive. Charcoal filters produce decreased H_2S deliveries and bisulfite used in tobacco processing is reflected in increased sulfur delivery by the resulting cigarettes.

As illustrated in Fig. 4, the gas phases of smokes contain a large number of other sulfur compounds. Approximately 28 peaks are observed using an FFAP column. Use of 1,2,3,4-tetrakis(2-cyanoethoxy)butane, an analog of 1,2,3-tris-

(2-cyanoethoxy)propane, the liquid phase employed by Groenen and Van Gemert[1], proved less successful than FFAP, yielding only 12 peaks. The larger number of components observed by Groenen and Van Gemert[1] may be a result of a difference in cigarettes or, as is likely from observations discussed above, artifacts of the sampling method.



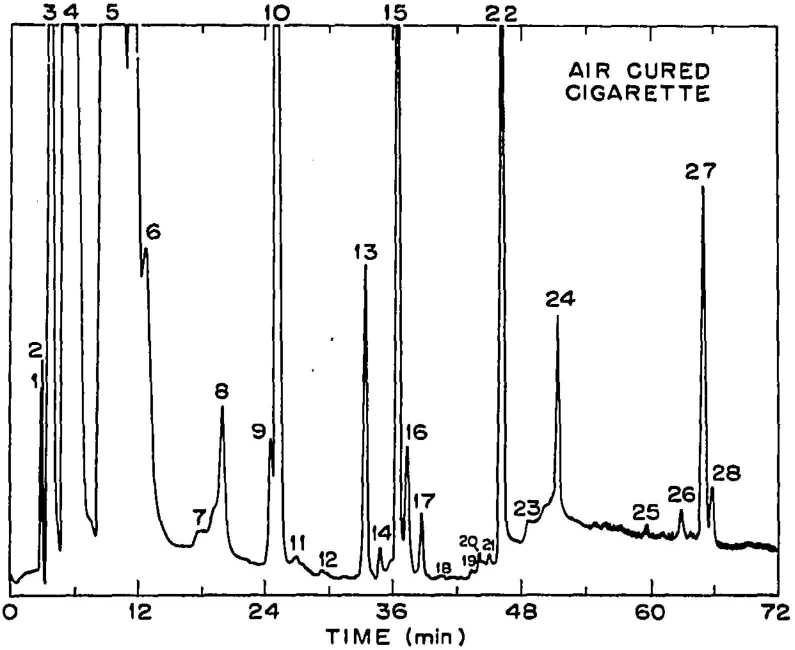


Fig. 3. Gas chromatogram of major sulfur compounds in the gas phase of cigarette smoke. Column, Tracor Special Silica. Nitrogen carrier gas flow-rate, 15 ml/min; temperature, 24 °C; sample size, 0.4 ml. 1 = COS (attenuation × 10^0); 2 = H_2S (attenuation × 10^0); 3 = CS_2 (attenuation × 10^4); 4 = SO_2 (attenuation × 10^4).

Fig. 4. Gas chromatographic profile of sulfur components in the gas phase of cigarette smoke. Column, Varian FFAP, 20% on 60–80 mesh Chromosorb WAW-DMCS. Nitrogen carrier gas flow-rate, 60 ml/min; temperature, 24 °C for 6 min, increase 4 °/min to 225 °C; sample size, 3.5 ml. Attenuation first 54 min, × 10^4; last 18 min, × 10^3. 3 = COS; 4 = dimethyl sulfide; 5 = H_2S; 6 = CS_2; 10 = dimethyl disulfide; 13 = thiophene; 15 = diethyl sulfide.

Although it is apparent that the sulfur component of smoke is much more complex than had been assumed, additional study is needed before the quantitative distribution of higher-molecular-weight components is confidently known. In the best of the systems used in this study, the Skinner valves and the gas sampling valves of both machines allow some contact with metal surfaces. Since some components (Table II) are seen to increase when a stainless-steel loop replaces the Teflon loop —the rest of the system remains Teflon— even this very brief opportunity for contact on passage through the valves may provide artifactual results.

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