

Measurements of Low Concentrations of Carbonyl Sulfide*

by

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INTRODUCTION

Carbonyl sulfide (COS) has been reported to be present in the gas phase of cigarette smoke in a concentration of 20–40 µg/cigarette (5, 11) or 150–500 µg/cigarette (10).

We have for some years been performing selective exposure experiments on rabbits for the study of the histotoxic lung effect and the atherogenic effect of gas phase components of tobacco smoke (6, 7, 8); the methods reported here to determine COS in air at concentration levels of up to 120 ppm were developed for use in our exposure studies with COS (9). These methods comprise: mass spectrometry (MS), gas chromatographic separation and electron capture detector method (GC/ECD), and measurements by a Beckman carbon monoxide infra-red analyzer (B-CO).

In the present study, GC/ECD appeared to be suited to the measurement of the COS content, both in mainstream and sidestream smoke from cigarettes; these measurements are reported here.

MATERIAL AND METHODS

An airtight exposure chamber with a volume of about 10 m³ (1) was used to obtain air with different COS concentrations. COS was delivered from a gas cylinder, passed through a rotameter and mixed with atmospheric air immediately before the entrance to the chamber. A constant flow rate of COS and atmospheric air was

maintained for 24 hours before air/gas samples were drawn from the middle of the interior of the chamber, by means of a reciprocator-type pump, for the determination of the COS concentration.

Mass Spectrometry

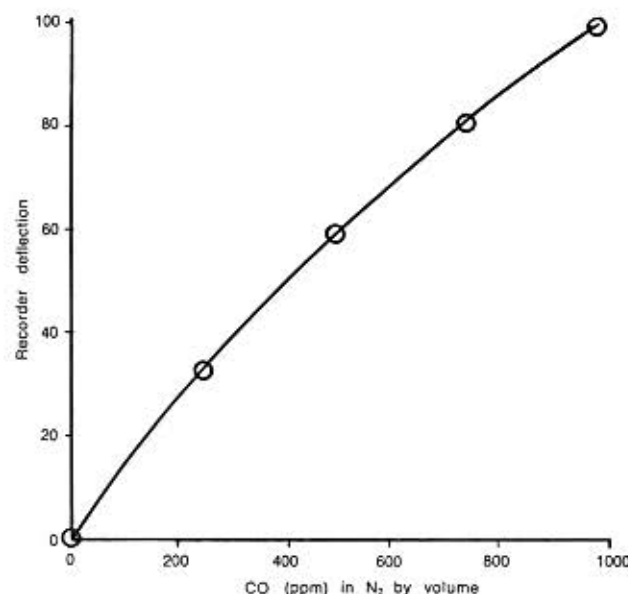
A Varian MAT CH 5D mass spectrometer equipped with a gas inlet system was used. The signals were detected by an electron multiplier. The temperature of the gas inlet system was 130 °C and the ion source 200 °C. Ionizing energy was 70 eV with 100 µA trap current. Resolution was approximately 1000. The gas samples were transferred from the exposure chamber to the mass spectrometer in 100 ml glass pipettes with stopcocks greased with Apiezon N. The mass spectra were obtained on an UV recorder (Fig. 5), whereas the two masses *m/e* 36 and *m/e* 60 corresponding to ³⁶Ar and the molecular ion of COS respectively were registered on a Honeywell recorder. The stable isotope ³⁶Ar at a concentration of 31.5 ppm in dry air (3) was used as internal standard.

Gas Chromatography

A 1 m stainless steel column (2 mm inside diameter), packed with Porapak QS (80–100 mesh), was connected to a Perkin-Elmer electron capture detector (⁶³Ni). High purity nitrogen was used as carrier gas with a flow rate of 50 ml/min. The system was operated at room temperature. A gas sample of 200 µl was injected by a Hamilton syringe through a silicone septum. The system was calibrated with samples of air containing a known amount of COS. These were prepared by injecting pure COS into 2 l volumetric glass flasks with rubber plugs.

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Figure 1. Infra-red analyzer calibration curve (Beckman).



Beckman CO-Meter

A Beckman infra-red analyzer, model 215, equipped for carbon monoxide (CO) determination, measured the content of COS in a continuous gas flow sucked from the exposure chamber by the reciprocator pump. The instrument was calibrated against normal air and air with 180 ppm CO (linear detection from 0–180 ppm CO, see Fig. 1).

COS Concentration in Cigarette Smoke

Cigarettes were mounted in a single port smoking machine (developed by *Artho and Koch, F. J. Burrus & Cie.*, Switzerland, cf. Fig. 2). By means of a Hamilton syringe, 200 μ l samples of mainstream smoke which had been passed through a Cambridge filter were drawn from the freshly generated smoke of the sixth puff (Fig. 3). Such samples were immediately injected into the GC/ECD.

To obtain corresponding measurements of sidestream smoke, 20 burning cigarettes mounted in a holder were

placed under a glass globe from which smoke samples could be drawn at the top with a syringe (Fig. 4). Measurements were performed on three commercial cigarette brands (A: strong, non-filter; B: medium, filter; and C: mild, filter cigarette), and also on three experimental cigarettes commercially produced (Molins Mark 8A and 9A machines) from pure, unflavoured tobaccos (D: flue-cured; E: sun-cured; and F: air-cured).

RESULTS AND DISCUSSION

A mass spectrum of a gas sample from the exposure chamber containing about 115 ppm COS is shown in Figure 5. In this figure, the upper half demonstrates the normal mass spectrum. In the case of the 5000 times amplification (lower half), it is seen that the signals of the molecular ions of COS at m/e 60 and of ^{36}Ar (31.5 ppm) at m/e 36 are very suited to determine COS in the range of 1–150 ppm. The response at m/e 64 is from SO_2 , which is a background impurity in the mass spectrometer. Gas samples of air without COS show a background response at m/e 60 corresponding to 10 ppm COS. However, at any time when the same air sample size was used and controlled by the signal of ^{36}Ar , it was possible to correct for this background and to measure the content of COS down to concentration levels of 1–2 ppm.

The sensitivity factor for Ar and COS was estimated by measuring samples of pure Ar and pure COS. The responses were expressed against the partial pressure in the gas inlet system.

To control the decomposition of COS, which might be caused by the use of uncoated glass pipettes (12), two experiments were performed at concentration levels of about 40 and 115 ppm respectively, by collecting the gas samples in the glass pipettes and in 5 l volume plastic bags (Saran). At the indicated concentration levels of COS, storage in Saran bags and glass pipettes for 1–8 weeks caused no changes in COS concentrations.

Figure 6 illustrates a calibration curve for COS obtained on the GC/ECD. At concentrations higher than 10 ppm, the curve flattens out. Therefore, in the range of 50 ppm

Figure 2. Cigarette mounted in filter holder which is connected to the smoking machine by a piece of rubber tubing.

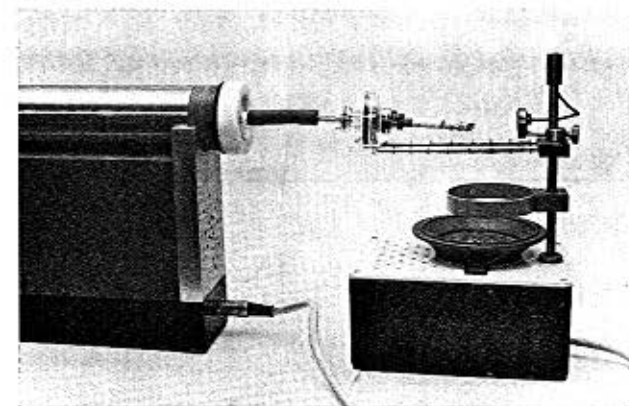


Figure 3. Sampling of mainstream smoke using a hypodermic needle and syringe. The rubber tubing is perforated with the needle and the smoke drawn into the syringe.

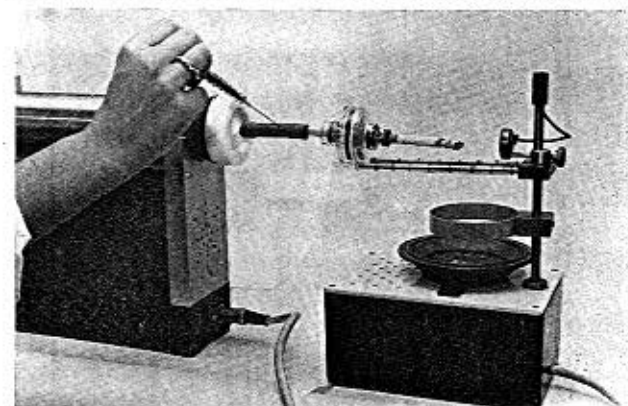
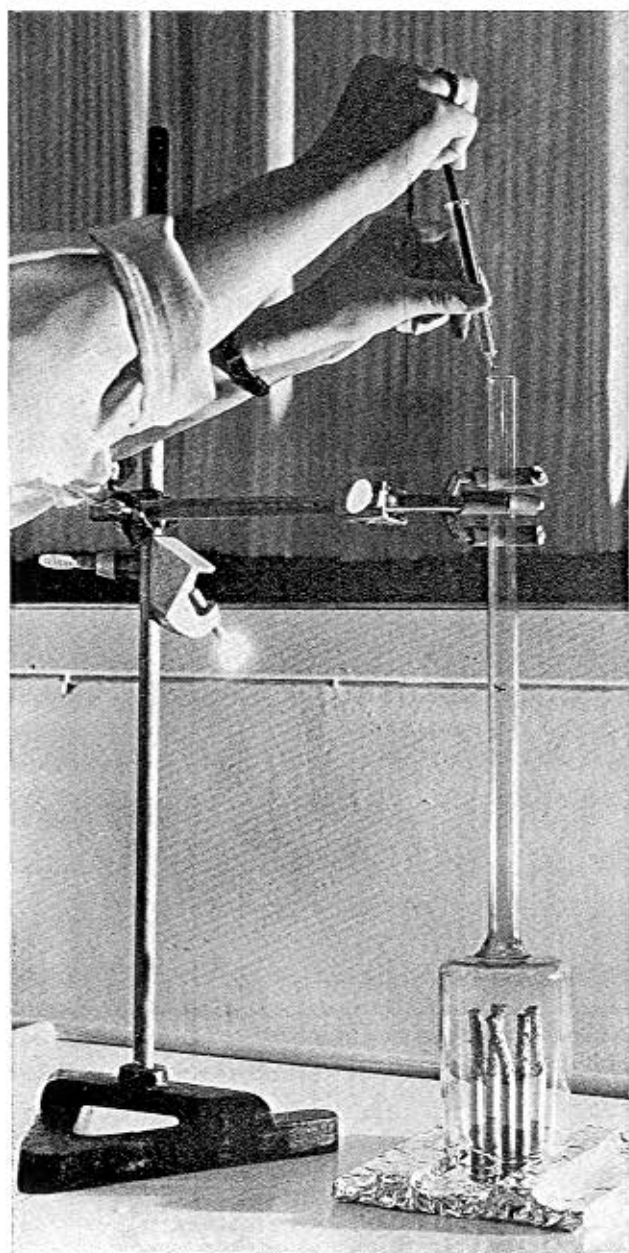


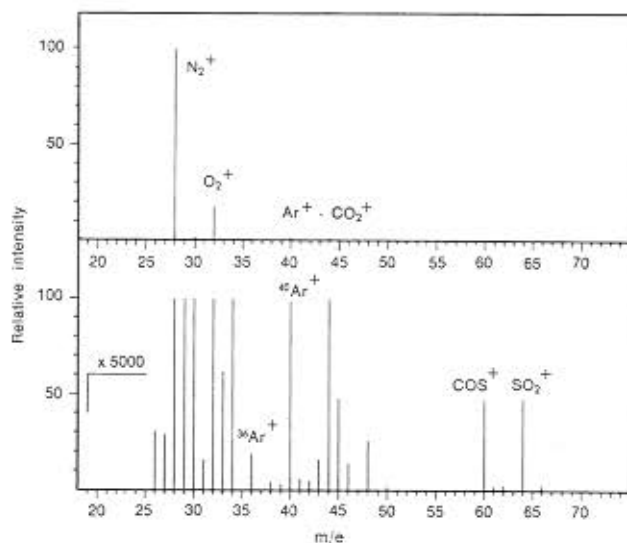
Figure 4. Sampling of sidestream smoke from the top of the "chimney". N.B.: In the illustration only 5 cigarettes are mounted in the cigarette holder. The photograph is from a subsequent experiment. The syringe is being removed after sampling of sidestream smoke.



it is possible, without diluting the air/gas sample, to estimate the amount of COS alone with an absolute certainty of about 5 ppm.

To compare the three analytical methods, air/gas samples were taken from the exposure chamber in immediate sequence and subsequently analysed by the B-CO, the GC/ECD and the MS. The results are shown in Figure 7 and Table 1. Because of the background effect, the COS values obtained by MS have a high degree of uncertainty in the range lower than 10 ppm, whereas the GC/ECD has a high degree of accuracy in this range (Figure 6). The COS values obtained by the B-CO are not absolute, since this apparatus was calibrated against CO and not against

Figure 5. Mass spectrum of an air sample containing 115 ppm COS.



COS. However, measurements of the B-CO against the MS demonstrated a linear response in the 10–120 ppm range. For obvious reasons (carbon monoxide), the Beckman CO meter is not suitable for measurements of COS in cigarette smoke.

Using the GC/ECD method, the results of measurements of the COS content of mainstream and sidestream smoke of the various cigarette types are shown in Table 2. The combination gas chromatography/mass spectrometry was used for qualitative identification of COS. COS concentrations of 25–30 ppm were found in commercial cigarette brands, while values of 25–60 ppm were obtained from the experimental cigarettes. These figures agree with those reported earlier by *Philippe et al.* (11) and *Horton et al.* (5), but are substantially lower than those reported by *Osborne et al.* (10). Measurements on sidestream smoke showed values eight to ten times lower than in mainstream smoke.

Figure 6. Calibration curve of electron capture detector for COS.

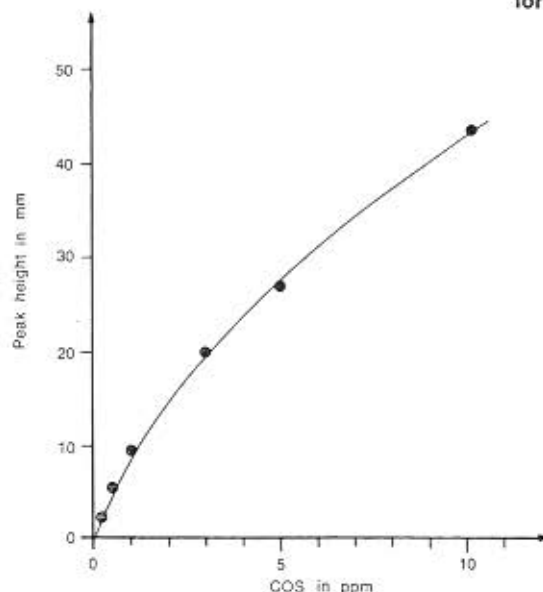


Figure 7. Comparison of COS concentrations determined by gas chromatography with an electron capture detector (GC/ECD), Beckman CO-meter (B-CO) and mass spectrometry (MS). Regression lines are shown (cf. Table 1).

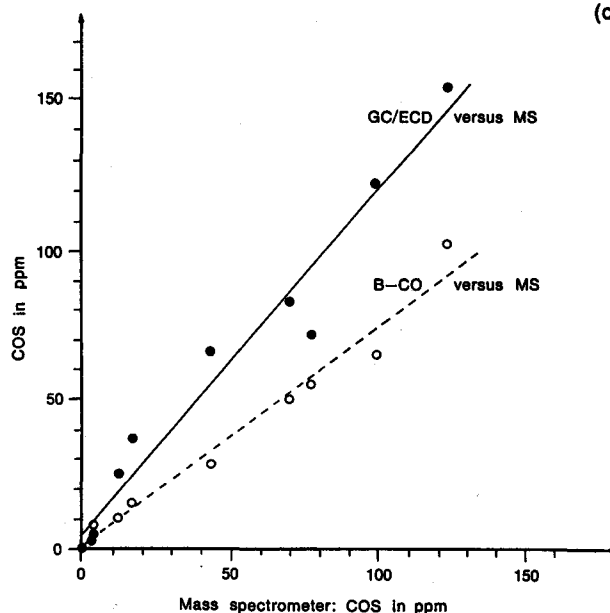


Table 1. Constants for the regression lines shown in Figure 7.

Analytical methods	Slope	Intercept (ppm)	Correlation
Gas chromatography with electron capture detector (GC/ECD) versus mass spectrometry (MS)	1.16	5.4	0.98
Beckman CO-meter (B-CO) versus mass spectrometry (MS)	0.74	0.2	0.99

Table 2. COS yield of different cigarette types.

	Cigarette type					
	A (strong)	B (medium)	C (mild)	D (flue-cured)	E (sun-cured)	F (air-cured)
Data						
Length (mm)	99	99	84	84	70	84
Circumference (mm)	24.8	25.3	25.0	25.1	25.2	25.2
Weight (mg/cigarette)	1383	1219	1048	1060	990	1040
Total particulate matter (mg/cigarette)	40-43	28-29	17-20	58	37	46
Nicotine (mg/cigarette)	2.7-3.0	1.9-2.0	1.1-1.2	2.7	1.9	2.6
Results						
Mainstream smoke:						
COS (ppm)	30	25	25	50	25	60
COS (µg/cigarette*)	21	18	18	35	18	42
Sidestream smoke:						
COS (ppm)	4	3	3	4	2	2

* Calculated values (1 cigarette: ≈ 8 puffs of 35 ml/puff).

Hoegg (4) has demonstrated that for most of the important constituents of tobacco smoke, the sidestream smoke yields are 3 to 4 times the quantity found in mainstream smoke. Recently Brunnemann et al. (2) demonstrated that HCN is an exception to this rule, since higher concentrations of HCN were found in mainstream smoke than in sidestream smoke. The present study demonstrates that like HCN, COS is substantially more abundant in mainstream than in sidestream smoke. Further investigations of COS in mainstream and sidestream cigarette smoke measured by gas chromatography with flame photometric detection are in progress.

SUMMARY

Three methods are described for measuring carbonyl sulfide at low concentration levels (1–120 ppm): mass spectrometry (MS), gas chromatography with an electron capture detector (GC/ECD) and measurements by a Beckman carbon monoxide infra-red analyzer (B-CO). When the results obtained by mass spectrometry were used as reference values the two other methods gave linear responses. The practical applicability for gas chromatography with an electron capture detector for measurements of the carbonyl sulfide content of mainstream and sidestream cigarette smoke is demonstrated. The values obtained revealed an approximately eight times higher concentration of carbonyl sulfide in mainstream than in sidestream cigarette smoke.

ZUSAMMENFASSUNG

Für die Bestimmung geringer Mengen (1–120 ppm) von Carbonylsulfid (COS) werden drei Methoden vorgestellt: Massenspektrometrie (MS), Gaschromatographie mit Elektroneneinfangdetektor (GC/ECD) und Messung unter Verwendung eines Infrarotanalysen-Meßgerätes für Kohlenmonoxid der Firma Beckman (B-CO). Unter Benutzung der durch Massenspektrometrie ermittelten Ergebnisse als Referenzwerte war die Anzeige der beiden anderen Verfahren linear. Es wird gezeigt, daß sich die gaschromatographische Methode unter Einsatz des Elektroneneinfangdetektors in der Praxis zur Bestimmung des Carbonylsulfidgehaltes des Haupt- und Nebenstromrauchs von Zigaretten eignet. Die Ergebnisse zeigen, daß im Hauptstromrauch etwa 8mal mehr Carbonylsulfid enthalten ist als im Nebenstromrauch.

RÉSUMÉ

On présente trois méthodes pour la détermination de petites concentrations de sulfure de carbone (1–120 ppm): spectrométrie de masse (MS), chromatographie en phase gazeuse avec détecteur de capture d'élec-

trons (GC/ECD) et mesure au moyen d'un analyseur Beckman infrarouge pour monoxyde de carbone (B-CO). Par rapport aux résultats obtenus par spectrométrie de masse, les deux autres méthodes donnent des réponses linéaires. On démontre l'applicabilité pratique de la chromatographie en phase gazeuse avec détecteur de capture d'électrons pour la détermination de la teneur en sulfure de carbone du flux principal et secondaire de la fumée de cigarettes. Il ressort des résultats obtenus que le flux principal contient environ 8 fois plus de sulfure de carbone que le flux secondaire.

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