PREPARATION OF HIGH PURITY CARBONYL[^{35}S]SULPHIDE

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SUMMARY

The title compound was synthesised by the reaction between elementary[^{35}S]sulphur and carbon monoxide at 300°C, and purified by passage over Porapak QS. The only detectable S-impurity in the purified product was CS_2 at <0.05% (v/v) of the COS concentration.

Key words: carbonyl sulphide, sulphur-35, GC purification

INTRODUCTION

The method described in this paper was developed to provide a simple means a producing carbonyl[^{35}S]sulphide (COS: carbon oxysulphide) for studies on uptake and metabolism by plants and soils [1]. An essential requirement of this work was that fumigations should be carried out with a COS concentration as close as possible to that of the ambient atmosphere (about 1.3 $\mu g\ m^{-3}$ [2,3]) in order to minimise the risk of phytotoxic effects. Previous measurements [4] of the deposition parameters of [^{35}S]COS to grass swards were made with low specific activity material which necessitated the use of much higher gas concentrations (about 13.4 $mg\ m^{-3}$) to enable the absorbed ^{35}S to be measured. The

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concentrations employed were so much greater than ambient that direct physiological effects on the plants could not be ruled out.

Other workers [4,5] have synthesised [^{35}S]COS by the action of sulphuric acid on potassium[^{35}S]thiocyanate, according to the equation:

$$KCN^{35}S + 2\ H_2SO_4 + H_2O \rightarrow \uparrow CO^{35}S + KHSO_4 + NH_4HSO_4$$

[^{35}S]KCNS was not available at the high specific activity necessary for our fumigation studies, and therefore an alternative synthetic route was sought. Since elementary[^{35}S]sulphur is available commercially at higher specific activity (up to 93 TBq g atom^{-1}, Amersham International plc, U.K.), this material was utilised in the method described here. The procedure depends on the reaction between elementary sulphur and carbon monoxide (CO), as described previously [6,7]. Contaminating CS_2 was removed from the crude product by selective adsorption on Porapak QS, and the purified [^{35}S]COS was diluted with N_2 to the required concentration before use in fumigation studies [1].

MATERIALS AND METHODS

[^{35}S]COS was synthesized in an all-glass reaction tube (volume about 16 cm^3) shown in Fig. 1. Elementary[^{35}S]sulphur in toluene (0.3 to 1.0 ml) (Amersham International, up to 185 MBq diluted with up to 1.75 mg carrier sulphur to produce the desired specific activity) was placed inside the main compartment (E) of the reaction tube. The toluene was evaporated at 40°C under reduced pressure. The vessel was flushed 10 times with CO by repeated evacuation and re-filling, and finally filling with CO to a pressure of 0.5 bar, before sealing the vessel at the constriction (F) by means of a propane-oxygen flame. A molar excess of CO over S was always present, and the initial pressure of CO was selected so that the pressure developed during heating did not exceed about 1 bar, so minimizing the risk of breakage.

The reaction of CO and S was performed under various conditions with the objective of producing an acceptable yield of [^{35}S]COS, and did not represent a quest for maximum reaction efficiency. Suitable conditions were found to be heating at 300°C for 20 h. Analysis of the crude product by high sensitivity gas chromatography (detection limit 7×10^{-3} ppm S) [8] showed that CS_2 was the only detectable impurity, representing about 5-10% (v/v) of the COS concentration. Previous studies [6,9] showed that CS_2 may arise from the thermal decomposition of COS at 200-300°C. However, CS_2 was removed easily from the crude product by selective adsorption on Porapak QS.

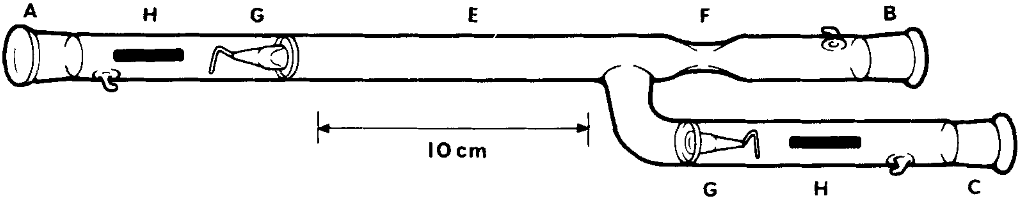

FIG.I REACTION VESSEL

Elementary[^{35}S]sulphur was deposited in compartment E and the vessel filled with CO via connection B. The vessel was sealed at constriction F. After reaction, the products were flushed out in N_2 introduced at C and passed out through A, after breaking the glass seals at G using glass-coated iron slugs (H). The vessel was constructed from borosilicate glass (1 mm wall thickness) with spring-secured B10/19 ground glass connections.

For routine preparation of high-purity [^{35}S]COS, the contents of the cooled (about 20°C) reaction vessel were flushed with O_2-free N_2 (flow rate 60 min^{-1}) through a glass column (90 cm × 4 mm internal diam.) containing Porapak ml (80-100 mesh). The short retention time of COS (about 4 min.) in the Porapak QS column, compared with >60 min. for CS_2, enabled an efficient separation to be made. The purified [^{35}S]COS emerging from the column was collected in a glass U-tube cooled in liquid N_2, and then flushed with N_2 into an evacuated aluminium gas cylinder after warming the trap to 40°C. Finally, the cylinder was filled with N_2 to the desired pressure. Analysis of the purified product showed that the CS_2 had been reduced to <0.05% (v/v) of the COS concentration. The ^{35}S concentration was measured by passing a sample of the gas through a combined scintillant-trapping solution consisting of 10:10:1 (v/v) xylene:ethanol:2-phenylethylamine, containing 5 g dm^{-3} of 2,5-diphenyloxazole and 0·05 g dm^{-3} of 1,4-bis(5-pheny-2-oxazolyl)-benzene, and counting the solution in an Intertechnique SL33 liquid scintillation counter. The trapping efficiency for $[^{35}S]COS$ was >99%.

RESULT AND DISCUSSION

The method described here provides a simple means at preparing $[^{35}S]$-COS at high purity and at a specific activity greater than that obtained from the hydrolysis of $[^{35}S]KCNS$ [4,5]. For present purposes, a specific activity of about 4 TBq $mole^{-1}$ was found to be suitable, but higher values can be obtained by using elementary$[^{35}S]$sulphur at higher specific activity.

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