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CONTINUOUS AND ULTRASENSITIVE APPARATUS FOR THE MEASUREMENT OF AIR-BORNE TRACER SUBSTANCES

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SUMMARY

An apparatus is described for the continuous and ultrasensitive measurement of air-borne tracer substances, based on direct analysis with an electron capture detector which uses ambient air as the carrier gas following the chemical conversion of indigenous oxygen to water. Optimal sensitivity and stability are achieved by the use of synchronous detection. The apparatus has potential application in the increasingly important study of the transport and diffusion of gases both on a local scale and over continental distances.

INTRODUCTION

The use of the electron capture detector with air as the carrier gas is hindered by atmospheric oxygen. The presence of this weak electron absorber, at a concentration of 21 % in the carrier gas is sufficient to cause a 94 % reduction in the detector saturation current[1]. Although the detector may function in this mode, the sensitivity and dynamic range are drastically reduced. An alternative approach which employs frontal chromatography coupled with electron capture detection for the semi-continuous determination of sulphur hexafluoride (SF_6) has been described by Dietz and Cote[2]. In this, the SF_6 is eluted in the nitrogen of the air for up to 60 sec before the oxygen emerges from the column.

The electron capture detector may be adapted, however, to operate as a continuous device by sampling air through a simple catalytic reactor where all substances other than nitrogen, carbon dioxide, SF_6 and some perfluorocarbons are converted to elemental hydrides. Atmospheric oxygen is changed to water, and chlorocarbons including the "Freons" produce HCl and HF, respectively, while nitrogen compounds are converted either to nitrogen or ammonia. Water formed in the reaction is removed conveniently by low-temperature condensation. The reactor, which is a palladium–gold alloy tube containing palladised asbestos, selectively transmits only SF_6 and some perfluorocarbons. This modified electron capture detector provides a continuous

signal in real time over the concentration range 10^{-9} to 4×10^{-14} parts by volume, without the need for chromatographic separation of SF_6 and oxygen[3-11].

EXPERIMENTAL

The general arrangement of the apparatus is illustrated in Fig. 1. In practice, air is driven into the apparatus from any convenient pump (A) at a flow-rate of 35–40 ml min^{-1}. A metal bellows pump (Model 21 E; Metal Bellows, Boston, Mass., U.S.A.) is an excellent non-contaminating pump for this purpose. A constant flow is achieved by metering the input air delivered by the pump through a control valve (B) (Type B1SA needle valve; Nupro, Cleveland, Ohio, U.S.A.). The incoming air is mixed with hydrogen gas supplied from a pressurized cylinder (C) and preset to flow at a rate of 20 ml min^{-1} via a capillary restrictor (D). The mixed gases then pass into the reactor (E), which consists of a palladium–gold (6:4) alloy tube 10 cm long × 3 mm in diameter (Englehard Ind., Cinderford, Gloucs., Great Britain). The reactor is heated electrically by means of an externally wound nichrome resistance heater (F) to a temperature of $300 \pm 20°$. The first 3.0 cm of the tube are loosely filled with 20% palladium on asbestos fibre (Englehard Ind.) which serves to combust the air–hydrogen mixture with the direct formation of water as steam. In addition, this catalyst promotes the conversion of all substances other than nitrogen, CO_2, and perfluorinated compounds to their elemental hydrides. Hydrogen in excess of that required for stoichiometric combination with oxygen and reduction of trace organics escapes through the walls of the reactor tube and is converted to water by catalytic reaction with atmospheric oxygen at the outer surface.

The gases leaving the reactor are a mixture of nitrogen, steam, traces of hydrogen halides, CO_2, and inert gases. This gas mixture is passed along a stainless-steel tube (0.159 cm O.D. by 0.76 mm I.D.) exposed to the air, in which it cools to about the condensation temperature of the steam. It is then passed into a 10 cm long
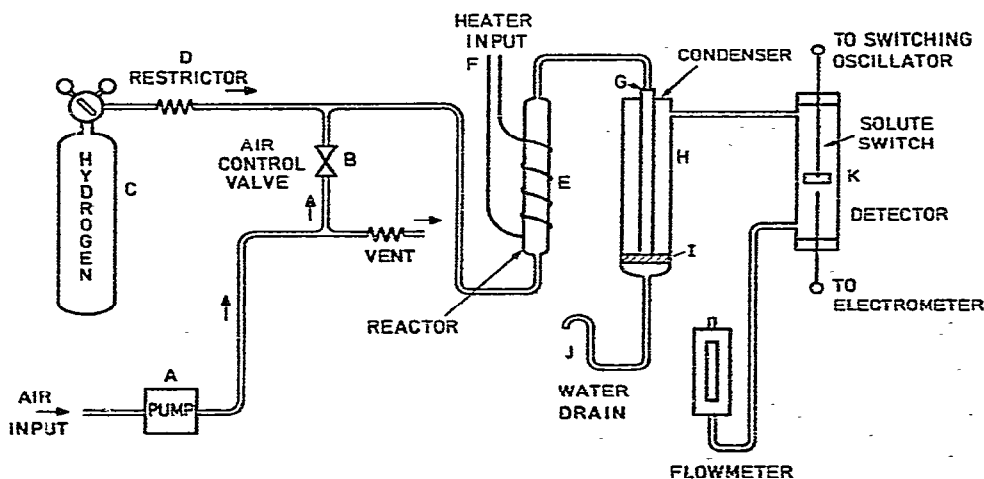

Fig. 1. Basic arrangement of continuous electron capture detection system.

× 3 mm diameter vertical pipe (G), which forms the inner member of a condenser, and is mounted axially inside a second pipe 6 mm in diameter (H). This outer pipe is firmly attached to a thermoelectric cooler (Model 801-2001-01; Cambion, Cambridge, Mass., U.S.A.) which is thermostatically controlled to maintain a temperature of approximately 3°.

The condensed water flows to a glass frit (I) (Sinterglass 531; Gallenkamp, London, Great Britain) which closes the bottom of the condenser. In this simple condenser system the water vapour is reduced in concentration to that set by the water vapour pressure at 3°. The bulk of the water which is condensed flows through the frit and away along a drain pipe (J) carrying with it, in dilute solution, the hydrogen acids and bases produced in the reactor. The capillary forces of the water in the pores of the frit are sufficient to seal the frit against the passage of gas. The gas stream leaving the condenser is now almost pure nitrogen with only the rare gases, CO_2 of the air, and traces of water vapour as contaminants. None of these react with or affect free electrons at thermal energy, and consequently this gas can serve as the background of an electron capture detector. When SF_6 is present in the gas stream it is detectable in the usual way by the capture of free electrons.

However, in the present apparatus a substantial gain in detectivity is achieved by passing the catalytically purified air into a specially modified electron capture detector (K), with solute switching and synchronous demodulation[12].

Electron capture detector with solute switching and synchronous demodulation

If the gas from the condenser is connected to a conventional electron capture detector, then it is only possible to observe trace concentrations down to about 1 in 10^{12} by volume. Noise and drift due to small changes of pressure, temperature, and gas flow-rate prevent the detection of even smaller concentrations. However, by using a solute switch[12], it is possible coherently to modulate the concentration of SF_6, for example, in the carrier stream, and then to recover any weak signals by synchronous demodulation. This not only provides a gain in detectivity but is impressively effective in eliminating baseline drift.
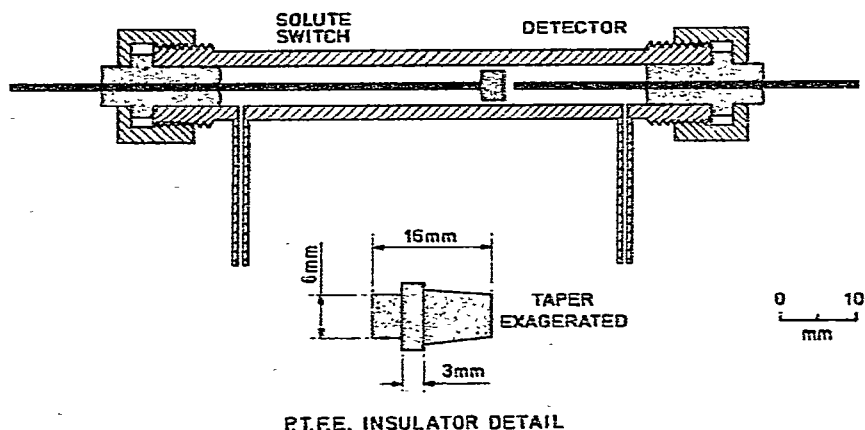
Fig. 2. Detail of dual-chamber electron capture detector with solute switching and synchronous demodulation.

The detailed design of the electron capture detector which incorporates these features is illustrated in Fig. 2. Two unequal chambers, in a ratio of 2:1, are provided in a single detector body by means of a PTFE separator. The detector is constructed from brass with PTFE insulators at each end and contains a single 300 mCi tritium radioactive source, size 5.0 × 1.5 × 0.025 mm thick (Radiochemical Center, Amersham, Great Britain). Gas from the condenser first enters the longer section of the detector, which operates as the solute switch. In this the SF_6 is alternately allowed to pass unhindered or destroyed by reaction with free electrons. The switch operates with an applied potential of 15 V positive, at a constant periodicity of 3 sec on and 3 sec off. The gas from the solute switch section of the detector passes around the PTFE separator and enters the shorter chamber which functions as a conventional electron capture detector. This senses the presence of SF_6 only when the switch allows it to pass, so that the output from this detector is therefore a low-frequency a.c. signal at the switching frequency. The amplitude of this signal is amplified fifteenfold and then converted to a steady d.c. level by means of a synchronous demodulator which is switched at the same phase and frequency as the solute switch. The basics of this electronic processing are illustrated in Fig. 3. The amplified signal is then passed through a low pass filter to remove any spurious noise generated by the switching process and continuously recorded to indicate the atmospheric SF_6 concentration. The entire system from the vapour switch to the output of the low pass filter achieves amplification of the SF_6 signal under conditions where noise and drift are rejected. Consequently the sensitivity of detection is increased by approximately 30 times, so that SF_6 can be detected at levels down to 4 parts in 10^{14} by volume.

Response to possible interferences

The ability of the apparatus to measure both continuously and specifically SF_6 and similar substances clearly depends on the special properties of the palladium catalyst and the temperature at which the reactor is operated, for there are various atmospheric contaminants which are also known to be strong electron absorbers. The most important class of electron absorbing trace compounds in the atmosphere are
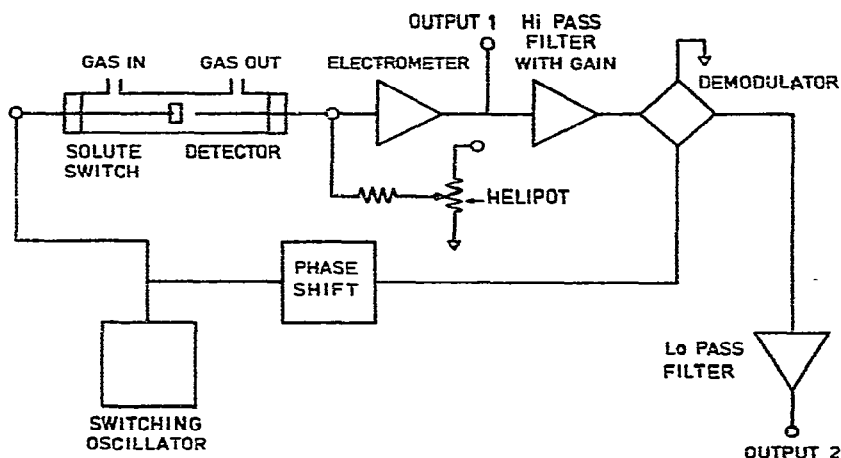

Fig. 3. Block diagram of electronic processing for dual-chamber electron capture detector.

TABLE I

RESPONSE OF CONTINUOUS APPARATUS TO POSSIBLE ATMOSPHERIC INTERFER-ENCES

Compound	Normal ambient conc. (ppt) [*]	Concentration of standard X (ambient conc.)	Instrument response
Freon 12 (CCl_2F_2)	115	7×10^6	$+$
		10^5	$-$
Freon 11 (CCl_3F)	87	5×10^7	$+$
		10^6	$-$
Freon 113 (CCl_2FCClF_2)	1	10^6	$+$
		10^5	$-$
CCl_4	138	10^8	$+$
		2×10^7	$-$
$CHCl_3$	19	1×10^5	$-$
CH_3CCl_3	75	5×10^5	$-$
$CHCl=CCl_2$	5	5×10^8	$-$
		10^{10}	$+$
$CCl_2=CCl_2$	21	5×10^6	$-$
		4×10^8	$+$

[*] ppt = parts per 10^{12} by volume.

the chlorocarbons and the chlorofluorocarbons ("Freons"). The high thermal and chemical stability of the Freons, in particular, suggests that they possibly might survive transport through the catalyst. To test for this possible source of interference high vapour concentrations of Freons and other industrial chlorinated solvents were injected directly into the apparatus. The results of these tests are listed in Table I, which also includes literature values for the global background concentrations of the substances tested[13,14]. None of the compounds listed in Table I gave a response at concentrations of 10^5 times their global background. However, dichlorodifluoromethane (Freon 12) and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) did give small signals when the concentration injected exceeded about 100 ppm and 1 ppm, respectively. Although this reflects the known stability of these particular Freons to palladium-type catalysts[15], it is anticipated that even higher concentrations of contaminants might be tolerated if the bed length of catalyst within the reactor were to be increased. In a second experiment to test the ability of the catalyst to continuously destroy unwanted Freon, several microliters of liquid Freon 11 (monofluorotrichloromethane) were added to a small room containing a high-speed fan to give an approximate vapour concentration of 1 ppm. The apparatus was then allowed to sample the air from this room at an input flow-rate of 40 ml min⁻¹ for about 45 min; and during this period there was no change in the baseline of the synchronously demodulated channel.

PERFORMANCE

The performance of the apparatus is illustrated in Fig. 4. Trace A is the output from the conventional pulsed detector electronics, while trace B is the synchronously
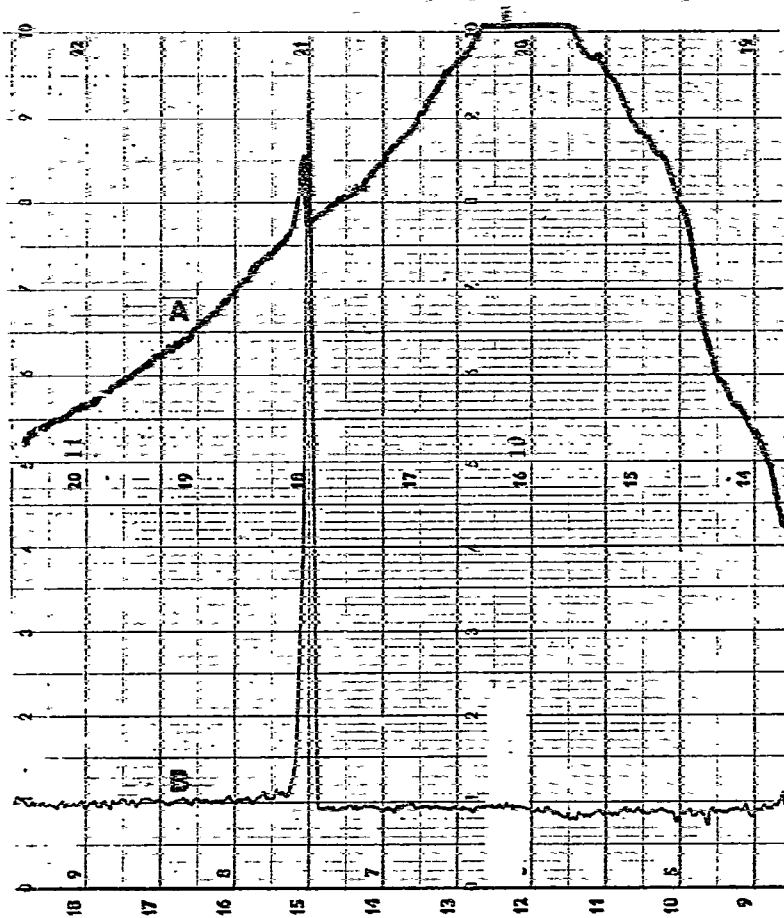
Fig. 4. Performance of continuous electron capture apparatus. Channel A: conventional pulsed detector output (4×10^{-10} A.f.s.d.); channel B: synchronously demodulated output (1.7×10^{-11} A.f.s.d.).

demodulated channel. The very stable baseline of this demodulated channel is particularly striking compared to trace A, where the baseline has drifted off-scale and back on again in response to a deliberately imposed change of about $10°$ in the ambient temperature of the laboratory. The 10 mV offset from electrical zero observed on trace B represents the normal background SF_6 concentration of approximately 5×10^{-13} by volume.

The signals observed on both channels are in response to a brief increase in SF_6 concentration to about 1 ppt (1 part in 10^{12} by volume). The substantial gain in sensitivity on the synchronously demodulated channel is readily apparent. Thus far the ambient background of SF_6 is small and steady enough in concentration not to interfere with the use of SF_6 as an air-borne tracer. The apparatus can also be used with perfluorocarbon tracers but the sensitivity to these substances is less than with SF_6.

The apparatus described thus provides both a continuous and ultrasensitive monitor which is also highly selective. The design is simple and is easily adapted as a self-contained portable instrument. It should find practical applications in the study of atmospheric dispersion problems, including hurricane dynamics, and the experimental verification of theoretical models which describe complicated patterns of air flow. Moreover, the basic apparatus should be useful in conducting long-range tracer experiments to study transport and diffusion of gaseous plumes over continental distances.

ACKNOWLEDGEMENT

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