

Notes

CHROM. 6211

Reactor or automotive effluent collector for chromatographic sampling

When the vapor of a volatile hydrocarbon is mixed with air and passed through an automotive engine a complex mixture of products is obtained. In a previous publication¹ we have investigated the oxidation of a normal pentane-air mixture in a tube reactor as a model to produce oxidation products over a wide range of reactor temperatures.

The compounds found on analysis were: (a) unchanged reaction products pentane, oxygen and nitrogen; (b) saturated hydrocarbons methane, ethane, propane and butane; (c) unsaturated hydrocarbons ethylene, propenes, butenes, and traces of pentenes; and (d) oxidation products including carbon monoxide, carbon dioxide, water, formaldehyde, acetaldehyde, propionaldehyde, 2-methyl tetrahydrofuran, formic acid and methyl alcohol. Polymeric substances could not be measured.

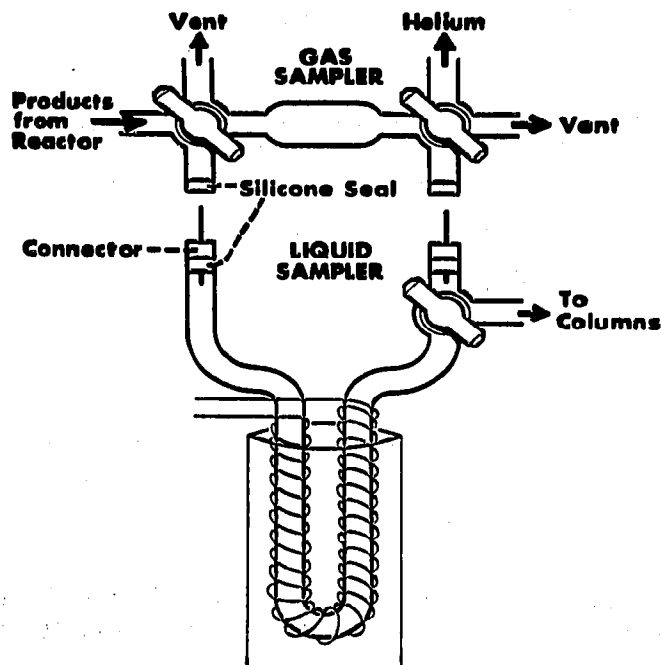


Fig. 1. Collection chambers for the samples.

Collection of a sample containing adequate amounts of all the pyrolysis and oxidation products is one of the most difficult problems in the study of automotive effluent. The products range from water to carbon monoxide to polycyclic hydrocarbons such as benzopyrene, and there is no analytical instrument available which will measure the concentration of each component accurately.

The sampling system to be outlined causes little interruption in the normal effluent flow. The column used to analyse the fixed gases, a Linde molecular sieve, would not separate the condensed substances and the column used for the condensed substances would not resolve the fixed gases. So we sampled the fixed gases and the condensed substances simultaneously and channeled them into separate columns.

Collection chambers for the samples are shown in Fig. 1. A suitable bent piece of Pyrex glass tubing wound with heating tape and loosely packed with glass wool is used to trap the liquids and condensable gases. The fixed gases are collected in the gas sampler bulb and in the tubing between the two four-way stopcocks and a three-way stopcock. The volume was found by previous calibration.

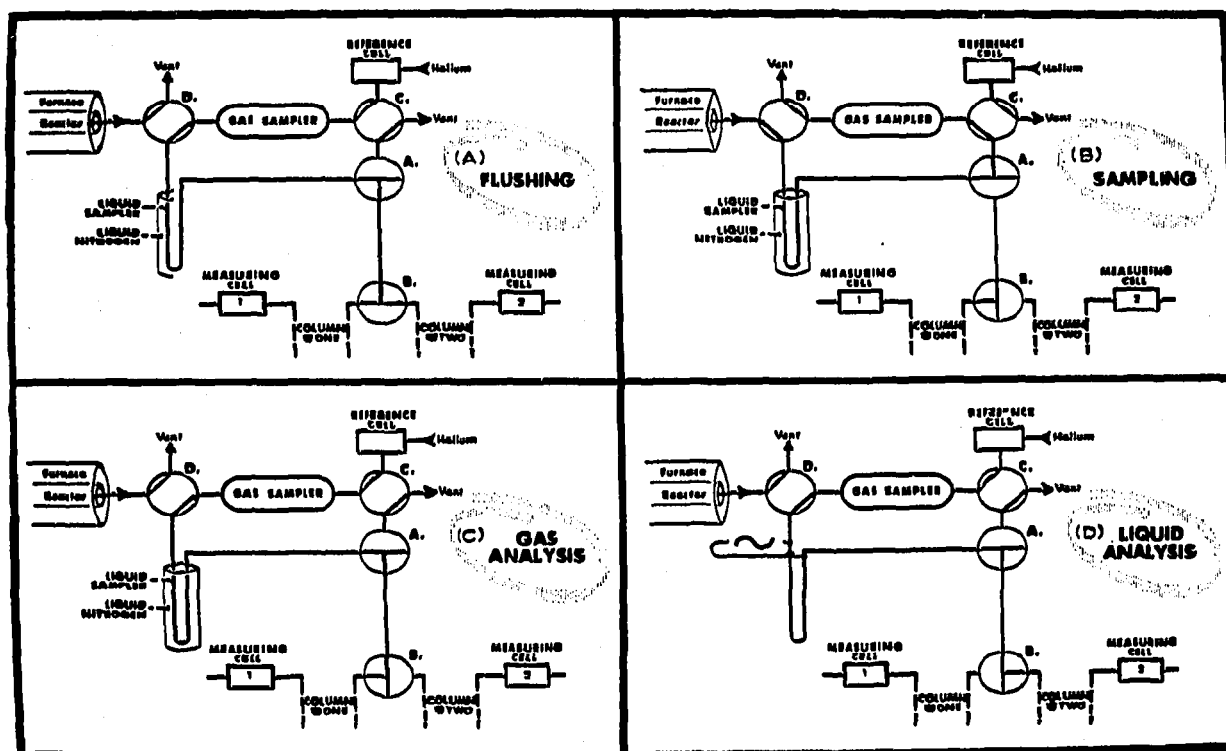


Fig. 2. Diagrams of the operation of the sampling system.

The operation of the sampling system is illustrated diagrammatically in Figs. 2A-D. Instead of a furnace reactor an automotive engine may be used, or for experimental purposes a single cylinder laboratory engine such as the Labeco. If an engine is used, part of the exhaust is sampled and the remainder goes to waste. During the flushing cycle helium circulates through the reference cell, the sampling apparatus and the columns. When conditions are ready for sampling a Dewar vessel containing liquid nitrogen is first introduced around the liquid sampler. This cools it in approximately 1 min. To sample the effluent, stopcocks A, B, C, and D are turned in that sequence. Sampling commences when stopcock D is turned and is continued for a predetermined period during which the exit flow-rate from the vent is measured.

At the end of the sampling period stopcock D is turned back, so that all the condensable products are trapped, together with a known volume of fixed gases.

By turning stopcocks A and C to the positions shown for gas analysis, the fixed gases are pushed by the carrier gas through the cold liquid sampler and on to column 1, which is packed with 5A Linde molecular sieve. When gas analysis is complete, stopcock B is turned so that carrier gas flushes column 2, which has a stationary phase of 25 % bis[2-(2-methoxyethoxy)ethyl] ether on 30-60 mesh firebrick. Liquid analysis is carried out by removing the liquid nitrogen and passing a suitable current through the heating tape.

An alternative means of completing the liquid analysis is to volatilize the nitrogen condensate onto the column at room temperature. After completion of the analysis the sampling tube is removed, washed out with cyclohexane and analyzed for polycyclic hydrocarbons and other less volatile substances by the method of COMMINS².

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1 S. SANDLER AND J. A. BEECH, *Can. J. Chem.*, 38 (1960) 1455.
2 B. T. COMMINS, *Atmos. Environ.*, 3 (1969) 565.

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