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EVOLVED GAS ANALYSIS USING THE PERKIN–ELMER TGA7 HT—A NOVEL METHOD OF GAS SAMPLING

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ABSTRACT

A novel method has been developed to perform evolved gas analysis using the Perkin–Elmer TGA7 HT. A gas sampling tube was fitted to the sample purge assembly with its tip 1 mm above the sample pan. With the gas outlet of the furnace closed, any evolved gases are swept by the carrier gas through the tube into a sample tube for later analysis. This method alleviates the problem of the large "dead volume" involved when using the normal gas outlet points of the furnace tubes.

INTRODUCTION

Thermal analysis combined with evolved gas analysis is not new and has been used for several decades. Various techniques are described in detail by Wendlandt [1]. The pneumatically operated furnace/sample tube assembly of the Perkin–Elmer TGA7 has produced a specific problem to the user who is interested in analysing the gases evolving from a thermal decomposition. The position of the normal gas outlet points of the furnace tubes (both the high temperature and standard temperature versions) is inconvenient as the "dead volume" involved is far too large to produce any meaningful result (see Fig. 1). A workable sampling method was introduced commercially by Perkin–Elmer for connecting the standard furnace version of the TGA7 to an infrared spectrometer (Perkin–Elmer Corp., Analytical Instruments, Norwalk, CT, U.S.A. Part no L1165050/1 TG-IR Interface 1700X).

In this paper we present a novel method of installing a gas sampling tube into the high temperature version of the Perkin–Elmer TGA7. The tube is stationary in that it does not form part of the pneumatically operated system. The tip of the sampling tube is situated within 1 mm of the sampling pan. By closing the normal gas outlet of the reactor tube with a piece of rubber tubing and a pinch-cock, all the volatile material is swept by the carrier gas into the sampling tube. This results in a minimal "dead volume" which can for all practical purposes be ignored. Depending on the carrier

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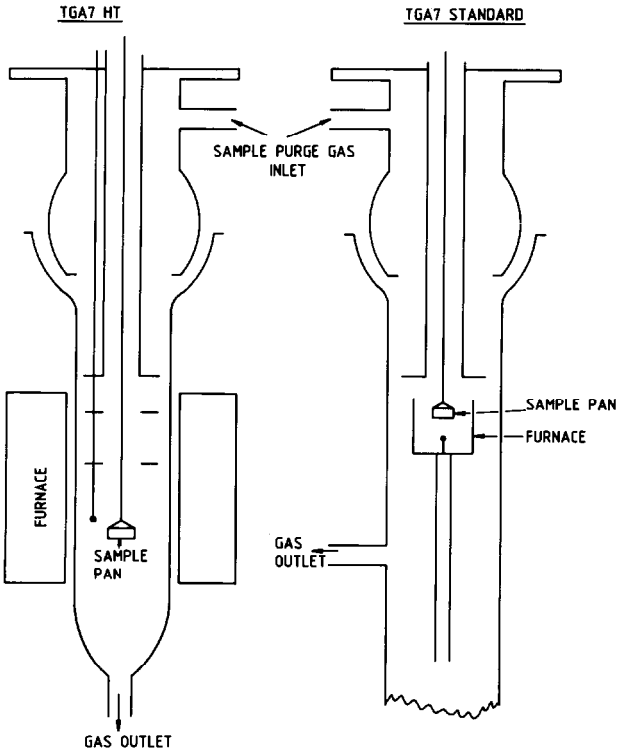

Fig. 1. Schematic layout of the two different furnace geometries available for the P-E TGA7.

gas flow and the length of the transfer line between the TGA and, e.g. a gas chromatograph (GC), the transfer time was calculated to be typically less than 1 s.

TECHNICAL DESCRIPTION

A detailed sketch of the instrumental lay-out is shown in Fig. 2. The description which follows refers to this sketch. The actual sampling tube (a) consists of a ceramic tube with an outside diameter of approximately 2 mm. This tube extends from the vicinity of the sample pan up into the cooler parts of the furnace tube. Here it is fixed into a 3.2 mm stainless steel tube (b) of a suitable internal diameter using epoxy glue. This stainless steel extension is threaded to fit into elbow (c). This elbow is silver soldered to a continuation of the 3.2 mm sample tube which then fits onto the main body (d) of the sampling unit. The main body of the sampling unit is made from a stainless steel "T" piece of an outside diameter similar to the glass sample purge gas inlet of the TGA system as supplied by Perkin–Elmer. The sampling tube passes through the "T" piece where it is sealed by silver-

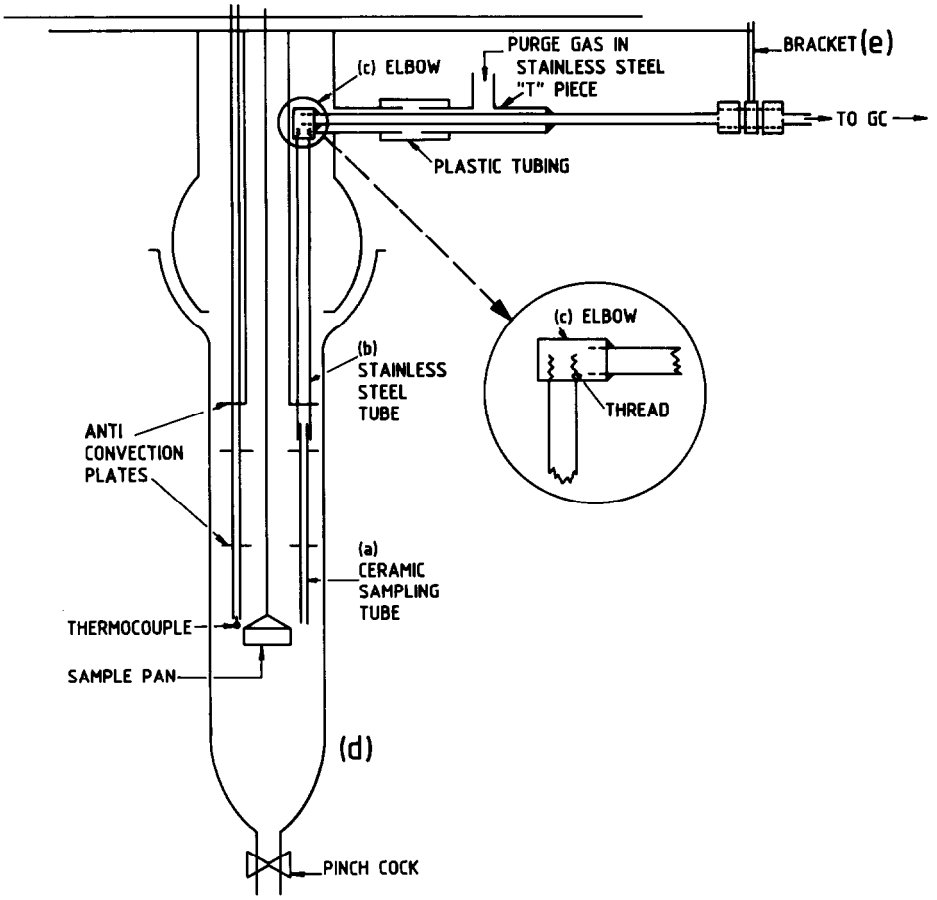

Fig. 2. Schematic layout of the modified version of the TGA7 as described in this article.

soldering it at the one end. The most critical part of the whole unit to manufacture is the elbow (c). This not only has to be threaded to accommodate the 3.2 mm stainless steel sampling tube, but has to be small enough to pass through the glass inlet tube. Enlarging this inlet tube by a glassblower would help in this respect although this was not attempted by us.

Installation is relatively easy. The only modification needed to the TGA system is the drilling of the necessary holes in the platinum and stainless steel anti-convection shields to accommodate the sample tube. The main body of the sampling system is connected to the gas inlet with the aid of a piece of plastic tubing. The existing plastic line which carries the sample purge gas is shortened and fitted over the side arm of the "T" piece. The ceramic/stainless steel sampling tube is now screwed through the anti-convection plates into elbow (c). PTFE thread-seal tape ensures a gas-tight connection. The length of the sampling tube can now be accurately determined with the sample holder of the TGA in position.

To prevent damage to the glass parts of the TGA and to make the whole unit more rigid, the 3.2 mm stainless steel line is fitted to a connector which in turn is fixed to the main body of the thermal balance with a bracket (e). From this connector, a suitable transfer line to any of a series of analysis systems (e.g. gas chromatography (GC), mass spectrometry (MS), Fourier transform infrared spectroscopy (FT-IR), etc.) could now be fitted. Our system did not make provision for a heated transfer line which may be necessary in some applications.

VERIFICATION OF THE SYSTEM

The system as described was connected to a Varian 3400 gas chromatograph as shown schematically in Fig. 3. The gas sampling valve was a Valco model ST 2n + 2 type with 10 sample loops of 1 cm^3 each. The calcium carbide "pre-column" shown was used to convert any water formed to acetylene for easier identification by GC.

The "quantitative correctness" was verified by decomposing chemically pure calcium carbonate in pure argon at a heating rate of 50 °C min^{-1}. Gas samples were taken at intervals as required, using the gas sampling valve. These were then analysed on the GC after completion of the TG run. The GC result is shown in Fig. 4 in comparison with the accompanying DTG curve of the decomposition reaction. Quantification of the GC results in

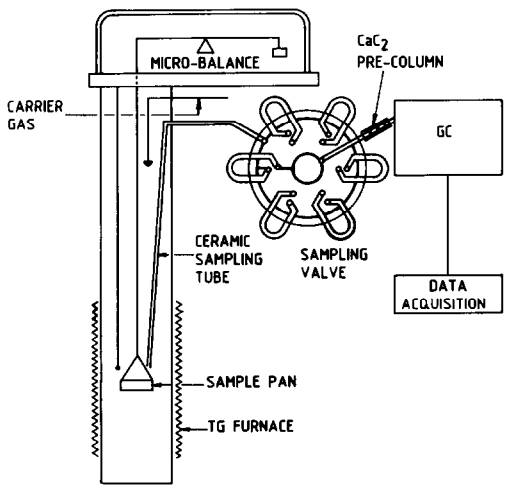

Fig. 3. Experimental layout of the TG–GC coupling.

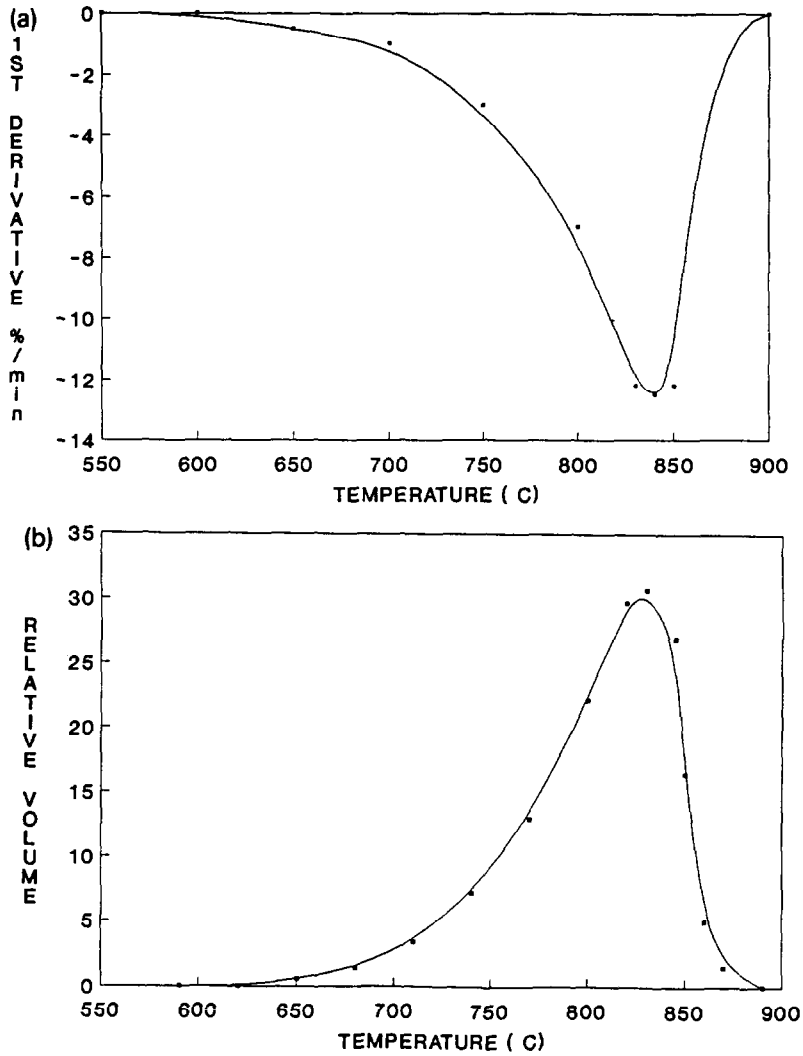

Fig. 4. Comparison of the rate of evolution of CO_2 from the thermal decomposition of $CaCO_3$ as detected by (a) DTG as well as (b) GC.

comparison with the TG result as well as the expected (stoichiometric) mass loss gave the following results:

Stoichiometric mass loss = 44.0%
Mass loss according to TG = 43.9%
Mass loss according to GC = 43.0%

A typical application in our laboratory is the analysis of light gaseous products evolved during the pyrolysis of coal. Figure 5 shows such a result which indicates the usefulness of TG–GC in this respect.

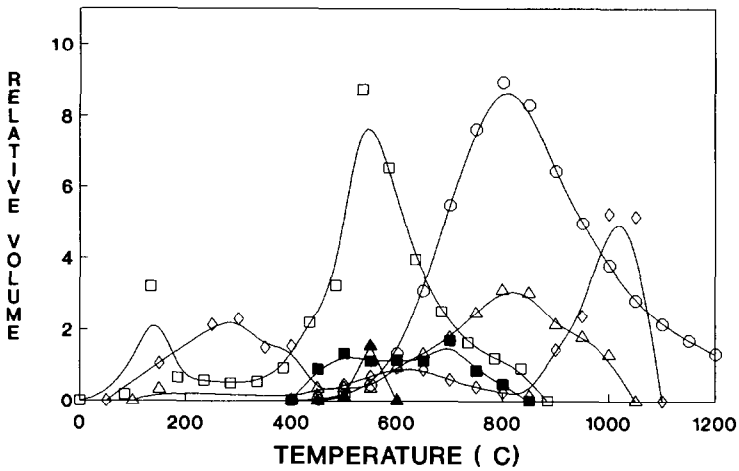

Fig. 5. Evolution of light gases during pyrolysis of a low grade South African coal type: □——□, water; ◇——◇, methane; △——△, carbon monoxide; ○——○, hydrogen; ■——■, carbon dioxide; ▲——▲, C_2.

CONCLUSION

A simple but useful technique of quantitative gas sampling in the Perkin–Elmer TGA7 HT has been devised which should be of value to thermal analysts using the same (or similar) equipment.

ACKNOWLEDGEMENT

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REFERENCE

1 W.W. Wendlandt, Thermal Methods of Analysis, 2nd edn., Chemical Analysis, Vol. 19, Wiley, New York, 1974, Chapter 8.