Journal of Thermal Analysis, Vol. 40 (1993) 993-998

CONTINUOUS DETERMINATION OF CARBON DIOXIDE EVOLVED DURING THERMAL DECOMPOSITION REACTIONS

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A simple device suitable for continuous monitoring of carbon dioxide evolved during thermal decomposition reactions is described. Carbon dioxide is transported by a carrier gas through the device connected to thermoanalytical equipment and absorbed by soda lime reagent. The reaction heat released is linearly proportional to the amount of carbon dioxide absorbed.

Keywords: detector cell for continuous determination of carbon dioxide, thermal decomposition

Introduction

Better understanding of thermoanalytical processes often necessitates use of evolved gas analysis (EGA) techniques to investigate the nature and amount of gaseous decomposition products. Carbon dioxide is one of the most frequently occurring decomposition products in thermoanalytical practice. Detection – and continuous monitoring – of carbon dioxide can easily be made with the two predominant EGA techniques, TG-MS [1] and TG-FTIR [2], but these require very expensive and complex instrumentation.

A large number of other methods is available for determination of carbon dioxide. Fibre-optic fluoro-sensors [3], amperometric [4, 5], conductometric [6] and potentiometric sensors [7] have all been used. Among the classical methods are the measurement of electrical conductivity of basic solutions absorbing carbon dioxide [8], measurement of heat conductivity [9], mass measurement after adsorption on a molecular sieve [10], and thermogastitrimetry [11]. The most common technique used for carbon dioxide determination is gas chromatography employing packed columns [12] with hydrogen, nitrogen, or helium carrier gas and FID or TCD detection.

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Akadémiai Kiadó, Budapest

The method described here provides continuous monitoring of carbon dioxide based on measurement of heat of reaction. The gaseous decomposition products liberated are transported by a carrier gas through a device packed with soda lime. The heat of reaction associated with the absorption of carbon dioxide is linearly proportional to the amount of CO_2 released. The design of the detector cell is very similar to those developed earlier for water and carbon monoxide monitoring [13, 14].

Experimental

The design of the carbon dioxide monitor is schematically shown in Fig. 1. The carrier gas with gaseous decomposition products enters the device at port 1 and leaves at port 2. The inlet port has an additional nozzle to introduce auxiliary wet gas, if necessary. The measuring cell (4) is packed with the reagent material (granules of soda lime). The reference cell (3) used to compensate temperature changes in the carrier gas is not packed, although the cell wall is covered by glass-fibre filter paper. The heat-sensing elements (8) and (9) are resistance thermometer coils (copper or platinum) connected to a bridge circuit. The operation of the device was tested by hypodermic needle injection of carbon dioxide into the carrier gas (nitrogen at a flow rate of 10 dm^3/h). The response curve obtained

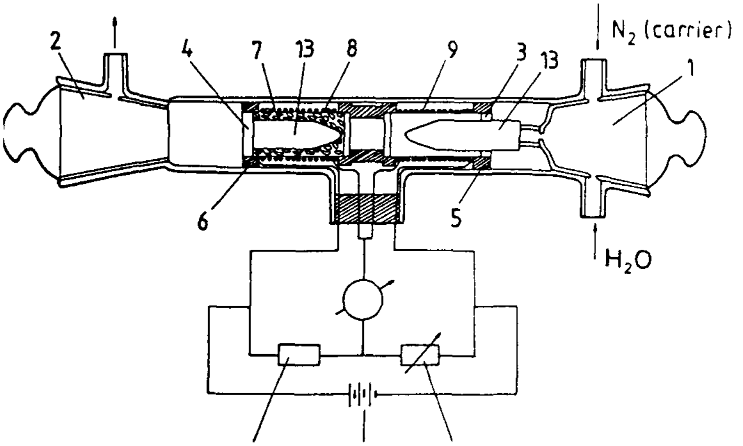

Fig. 1 Construction of the CO_2 monitor. 1: inlet stopper, 2: outlet stopper, 3: reference cell (silver), 4: measuring cell (silver), 5, 6: teflon support, 7: soda lime, 8: heat-sensing coil, 9: heat-sensing reference coil, 10: resistor, 11: variable resistor, 12: power source, 13: glass cone

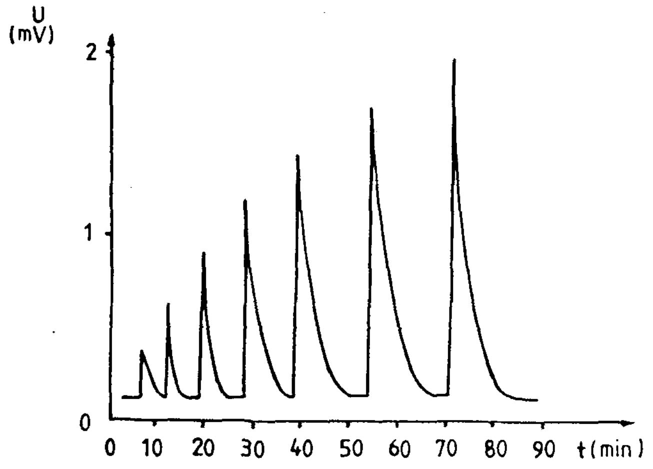

Fig. 2 Response curve obtained for 1 to 7 cm^3 CO_2 injected

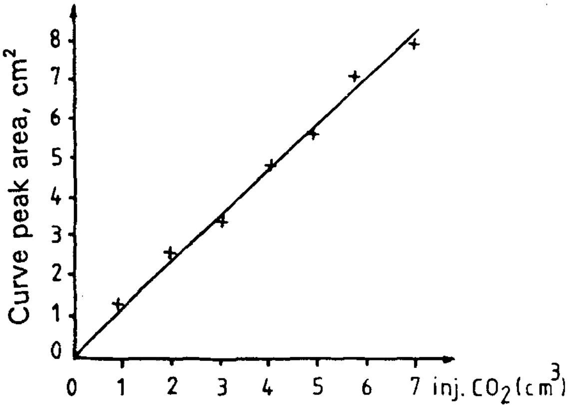

Fig. 3 Peak areas *vs.* injected volumes of CO_2

for 1 to 7 cm^3 carbon dioxide injected in series is shown in Fig. 2. Peak areas are plotted against amount of carbon dioxide injected in Fig. 3, and indicate the linear behaviour of the device (linear regression coefficient 0.99). In order to investigate reproducibility, injections of 1.0 cm^3 of carbon dioxide were made in series (Fig. 4). Differences between peak areas of two subsequent injections were less than 10%, indicating the semi-quantitative nature of the method.

The amount of reagent material was about 1.5 g. The absorption capacity of soda lime is 30–35% CO_2 (w/w), and thus the cell could in theory be loaded with 450–500 mg (250–280 cm^3) of carbon dioxide before replacement of the reagent is necessary. After introduction of 10 cm^3 CO_2, however, a gradual decrease of the peak height is shown, which could be due to crust (carbonate) formation on the surfaces of the particles. This problem can be eliminated by the introduction of wet auxiliary gas (water-saturated nitrogen, or air at a flow rate of 2 dm^3/h). No

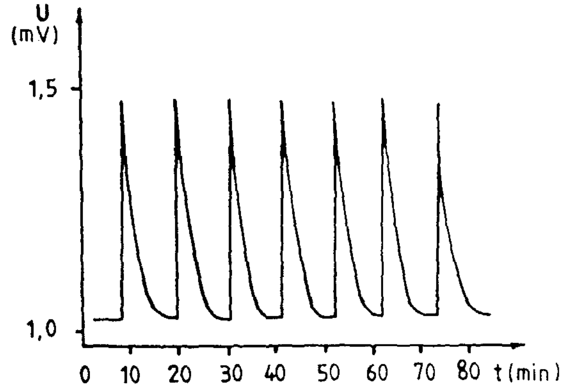

Fig. 4 Reproducibility test. Curves obtained for 1.0 cm^3 successive injections of CO_2

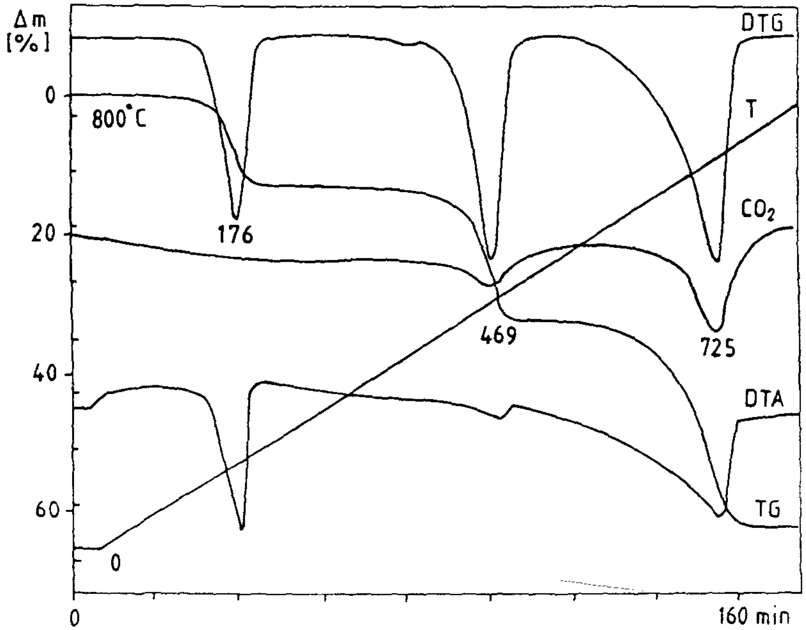

Fig. 5 Thermoanalytical curves for 27.02 mg $Ca(COO)_2H_2O$ in N_2 atmosphere together with the evolved CO_2 trace

decrease in peak height was observed after more than 50 injections (90 mg CO_2). As an alternative, fibrous anion-exchange resin reagent 'FIBAN' in OH^- form (courtesy of Prof. V. S. Soldatov [15]) was also investigated. This type of ion-exchange resin can successfully be used to remove acidic impurities (SO_2, H_2S, etc.) from air or stack gases. The sensitivity of the ion-exchange reagent was comparable with that of soda lime, but the capacity of the bed, however, was much lower (after the introduction of about 5 mg CO_2 the packing had to be removed for regeneration).

For thermoanalytical measurements the device (with soda lime reagent) was connected to a Derivatograph C type instrument (Hungarian Optical Works, Budapest). The evolved gases were collected in the furnace chamber of the derivatograph and transported through the detector cell by the carrier gas (nitrogen at a flow rate of 10 dm^3/h). Water-saturated nitrogen (2 dm^3/h) was introduced via the auxiliary inlet nozzle. The thermal decomposition curves of 27.02 mg $Ca(COO)_2H_2O$ (as model compound) and corresponding evolved carbon dioxide trace are given in Fig. 5.

The evolved carbon dioxide trace shows a large peak at 725°C. A small amount of carbon dioxide is also formed during carbon monoxide liberation (469°C). This is due to the partial disproportionation of carbon monoxide in an inert atmosphere according to the following reaction:

$$2CO = C + CO_2$$

The linear behaviour of the device was maintained during thermoanalytical investigations. The lowest detectable amount of CO_2 was about 0.2–0.5 mg, depending on the rate of evolution.

Selectivity

Organic cracking products, water, carbon monoxide and nitrogen monoxide do not appear to disturb the operation of the detector. Gas products of an acidic character (e.g. SO_2, SO_3, NO_2), however, do interfere. For practical applications these interfering gases can be removed from the carrier gas by various packings (e.g. activated carbon) placed between the cell and the thermoanalytical equipment, without loss of the relatively inert carbon dioxide.

The detector has already been successfully used – together with the H_2O and CO monitor – for studies of the decomposition mechanisms of transition metal oxalate [16] and clay-organic complexes [17, 18].

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Zusammenfassung — Es wird eine einfache Apparatur zur kontinuierlichen Beobachtung der Kohlendioxidfreisetzung bei thermischen Zersetzungsreaktionen beschrieben. Das Kohlendioxid wird mittels eines Trägergases in die am thermoanalytischen Gerät angeschlossene Apparatur transportiert und mittels Natronkalk absorbiert. Die freigesetzte Reaktionswärme ist der absorbierten Kohlendioxidmenge direkt proportional.