CONTINUOUS DETERMINATION OF CARBON MONOXIDE EVOLVED DURING THERMAL DECOMPOSITION REACTIONS

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A device suitable for the continuous detection of carbon monoxide evolved during thermal decomposition processes is described. The detector can be connected directly to thermoanalytical equipment of controlled gas atmosphere. Carbon monoxide collected by the carrier gas is passed through the device containing hopcalite catalyst. In the presence of oxygen carbon monoxide is converted to carbon dioxide in the cell and the temperature change caused by the heat of reaction is measured. According to experience, the change of temperature is linearly proportional to the amount of carbon monoxide released.

The signal curve of the detector can be compared to the simultaneously recorded thermoanalytical curves and used to determine the step in which carbon monoxide was released.

The detector is not completely selective to carbon monoxide, but in most cases the interferring gases can be removed from the carrier gas by various packings placed between the detector and the thermoanalytical equipment.

The use of evolved gas analysis (EGA) techniques in thermal analysis of various solid materials is of high importance in the determination of the nature and amount of volatile products formed upon heating.

Carbon monoxide is one of the products often formed in thermal decomposition of various organic and inorganic substances. The EGA methods currently available for the continuous determination of carbon monoxide are either expensive (TG-MS [1], TG-FTIR [2]), or indirect (thermogas titrimetry, TGT [3]) ones.

In practice a great variety of methods is used for the determination of carbon monoxide in gases. These methods (techniques) can be classified as chemical methods [4], spectrophotometric and colorimetric methods [5-7], conductivity measurements [8], infrared spectrophotometry [9-12], coulometry [13], voltametric methods [14], thermometric methods [15, 16],

gas chromatography [17-20], mass spectrometry [21-23], and carbon monoxide solid state sensors.

Listed among the carbon monoxide solid state sensors are tin(IV) oxide sensors [24-26] (conductance measurements), solid electrolyte sensors [27-29] (electromotive force measurements), zink oxide single crystal sensors [30] (the change in conductivity caused by CO adsorption is measured), proton-conductor sensors [31], and metal oxide semiconductor sensors [32, 33]. Although most of these methods are very powerful ones and can successfully be used for the solution of given problems, their direct application for the continuous monitoring of CO formed in thermoanalytical processes is rather limited due to various reasons (non-linear response, low sensitivity, lack of selectivity, etc.)

The device introduced here offers a simple, easy determination of carbon monoxide. The decomposition products collected by the carrier gas are passed through a glass cell packed with hopcalite catalyst. Carbon monoxide is converted to carbon dioxide at room temperature in the presence of oxygen. The heat of reaction is linearly proportional to the amount of CO released.

The detector signal is simultaneously recorded along with the thermoanalytical curves.

Experimental

Preliminary experiments were carried out by introducing carbon monoxide into a flow of oxygen passing through two cells (measuring and reference ones) connected in series. The schematic diagram of the apparatus used is shown in Fig. 1. A controlled flow of oxygen (at a flow rate of 100 cm^3/min) was led through a 6-port gas chromatographic switching valve (4) then the reference (10) and measuring (12) cells. The measuring cell was half-filled with hopcalite catalyst (11). In the other half of the cell a resistance thermometer (coil) was placed connected to a Wheatstone bridge. The reference cell was of similar design containing granulated marble as an inert filling material (9). The bridge was supplied by a stabilized power source (15) with 0.5 V DC, and the output signal caused by the temperature difference between the cells was fed into a computer through an A/D converter and an interface.

Two types of experiments were carried out using this set-up. In position 1 of the switching valve (solid line) CO (at a flow rate of 2 cm^3/min) was fed into the flow of oxygen by closing valve (7) and opening valve (6) after a

stable baseline was attained) for 5 minutes to investigate the response of the device for a step-function of 2% CO (V/V). The recorded curve (displayed on the monitor) is shown in Fig. 2.
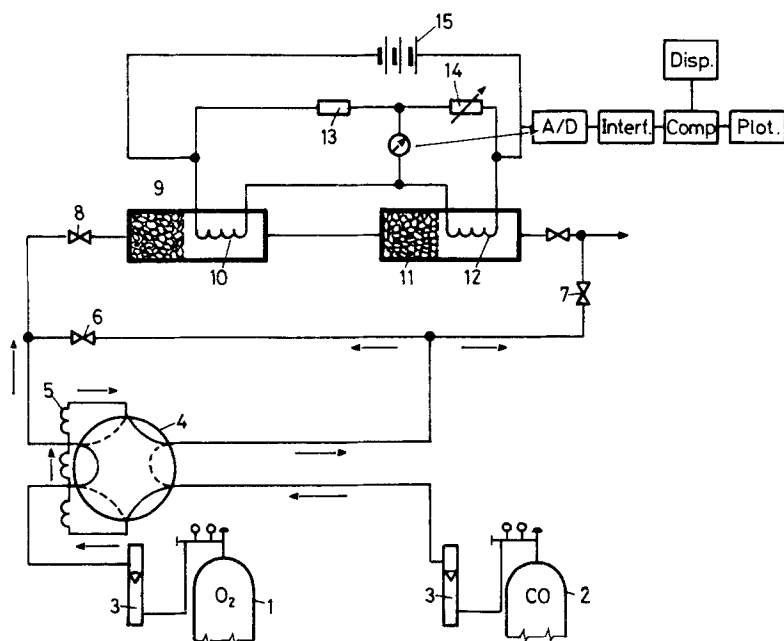

Fig.1 Schematics of the apparatus used for carbon monoxide detection experiments. 1: oxygen cylinder, 2: carbon monoxide cylinder, 3: flow meters, 4: switching valve, 5: empty GC colunm, 6: valve, 7: valve, 8: valve, 9: unert granule bed, 10: reference cell, 11: hopcalite catalyst bed, 12: measuring cell, 13: resistor, 14: variable resistor, 15: power source
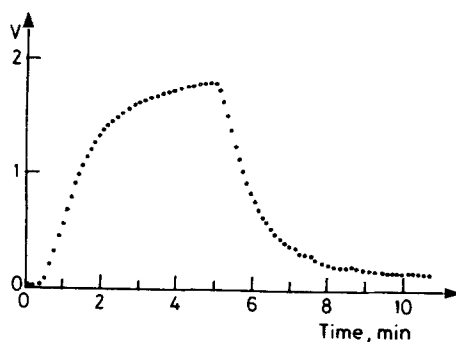

Fig. 2 Response curve for a step-function of 2% (V/V) carbon monoxide

In position 2 of the switching valve (broken line) and with valve (6) closed samples of carbon monoxide were injected into the oxygen carrier gas from 1 cm^3 to 5 cm^3 (depending on the volume of the empty stainless steel column used) to detect CO-plugs in the carrier gas.

In order to determine the dead-time and the time constants of the detector a computer analysis of the recorded curves was carried out by the constrained Nelder-Mead method [34]. Considering the figures obtained (dead-time is 6 seconds, time constants are less than 100 seconds) the device - in principle - was found to be suitable to follow CO concentration changes in the carrier gas during a thermoanalytical measurement. The signal to noise ratio, however, was high, and the device was very sensitive to small changes in the carrier gas flow rate. Therefore, a different configuration of the detector cell had to be designed to meet the requirements of simultaneous thermal analysis.
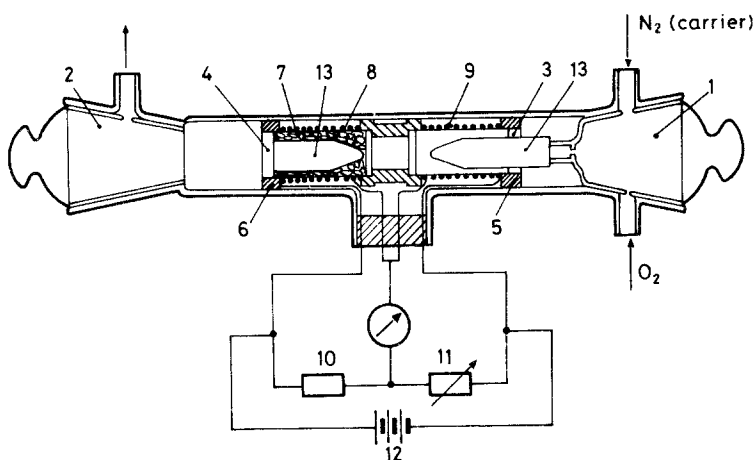

Fig. 3 Schematic diagram of the carbon monoxide detector. 1: ground glass inlet stopper, 2: ground glass outlet stopper, 3: reference cell (silver, cylindrical), 4: measuring cell (silver, cylindrical), 5, 6: teflon supports, 7: hopcalite, 8: heat sensing coil, 9: heat sensing reference coil, 10: resistor, 11: variable resistor, 12: power source, 13: glass cone

The schematic diagram of the final version of the CO detector is shown in Fig. 3. Nitrogen carrier gas mixed with gaseous decomposition products enters the device at port 1 (ground glass stopper) at a flow rate of 10 dm^3/h. At the same time oxygen (10% of the carrier gas) is also introduced. The gas mixture leaves the device at port 2. The measuring cell (4) is packed with hopcalite catalyst (7), while the inner wall of the reference cell (3) is

covered by glass fibre filter paper. The temperature of the cells is sensed by resistance thermometer coils (8) and (9). Since the coils are connected in series-opposition, the temperature changes of the carrier gas can be compensated.

The operation of the detector was tested by CO injections. Oxygen flow of 10 dm^3/h was led through the device and 0.2 cm^3 of CO (from a lecture bottle) was injected into the carrier gas through a silicon rubber septum. The amount of CO injected was increased in equal steps of 0.2 cm^3 up to 1.0 cm^3. In this way five curves were recorded as shown in Fig. 4. The areas under the curves were determined by integration and shown in the function of the injected volumes of CO in Fig. 5. It was stated that the device has linear characteristics which is an essential requirement for a simultaneous EGA monitor. Calculated by the least squares method, a linear regression coefficient of 0.994 was obtained.
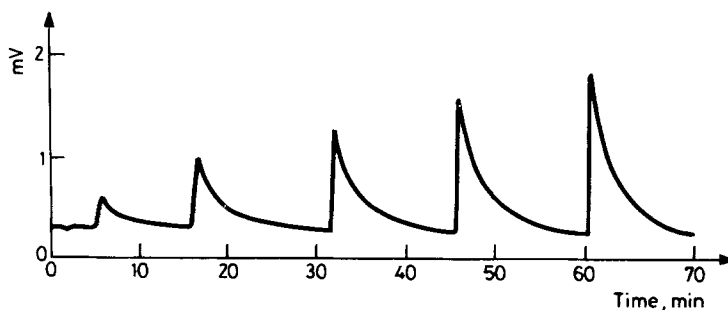

Fig. 4 Response curves obtained by carbon monoxide injection. Initially 0.2 cm^3 was injected, and its amount was increased by equal steps of 0.2 cm^3 up 1.0 cm^3

For further tests the detector was connected to a Derivatograph C type thermoanalytical instrument (Hungarian Optical Works, Budapest). The evolved gases were removed from the furnace chamber of a derivatograph and transported through the detector by the carrier gas (nitrogen at a flow rate of 10 dm^3/h). Oxygen was introduced (at a flow rate of 2 dm^3/h) at the inlet port of the detector. An absorber packed with P_2O_5 was placed between the derivatograph and the detector to remove water vapour (the adsorption and desorption of water in the measuring cell can interfere the measurements). The thermoanalytical curves of 45.65 mg of $Ca(COO)_2.H_2O$ including the simultaneously recorded signal of the CO detector are shown

in Fig. 6. By comparing the decomposition curves, the following conclusions can be drawn regarding the signal of the detector:
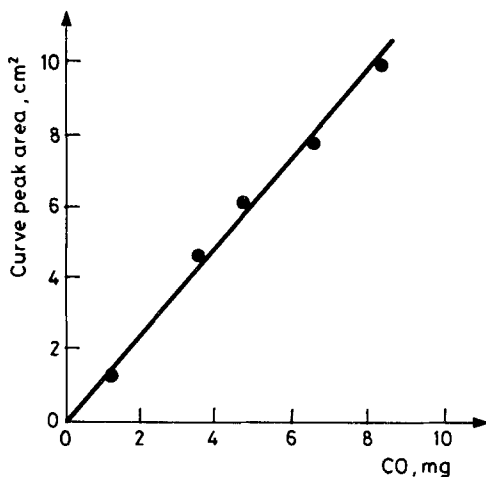

Fig. 5 The areas enclosed by the curves plotted against the injected volumes of carbon monoxide

1. The signal of the detector can closely follow the changes in concentration of CO of the carrier gas (i.e. the shape of the DTG peak at 478°) with negligible time delay.

2. All the points of the curve produced by the detector are proportional to the actual concentration of CO in the carrier gas and very close in time to the thermoanalytical curves.

The measurements were repeated with different amounts of $Ca(COO)_2.H_2O$. The relationship between the curve peak area and the mass of carbon monoxide released was linear as in the case of Fig. 5.

The lowest detectable amount of CO was found to be in the range of 0.1 to 0.5 mg, depending on the rate of the decomposition process.

Selectivity tests

In order to investigate the selectivity of the detector, the response of the device to various gases obtained from lecture bottles was studied using the injection method. Among the gases studied were methane, ethane, PB-gas, SO_2, H_2S, NO_x and NH_3. It was found that methane and low molecular weight hydrocarbons practically did not interfere.
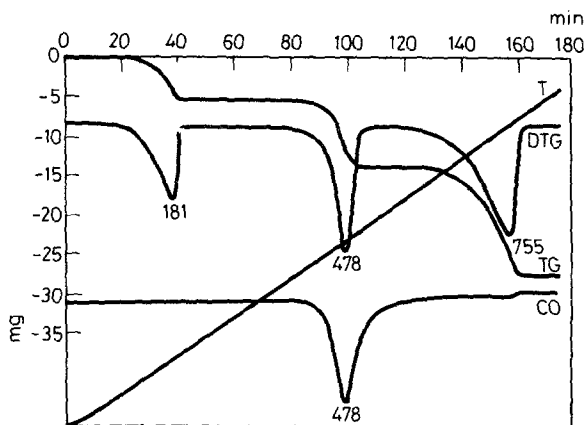
Fig. 6 Thermal decomposition curves of 45.65 mg Ca(COO)$_2$.H$_2$O, including the signal of the carbon monoxide detector
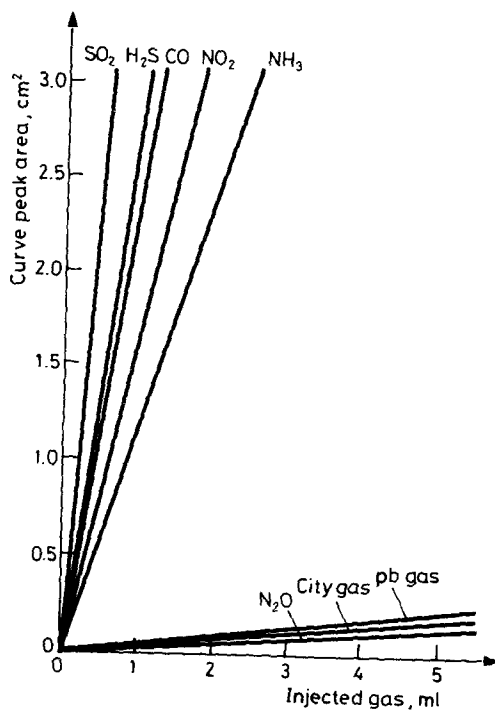

Fig. 7 Response curves obtained for various gases

However, SO_2, H_2S, NO_2, and NH_3 show severe interference (See Fig. 7) which can be attributed to their oxidation or adsorption properties. These gases, however, being highly reactive ones can be removed from the carrier gas by the use of various packings placed (in glass tubes) between the detector and the thermoanalytical equipment without any loss of CO.

The detector proved to be a proper tool for the continuous determination of carbon monoxide. Before the measurements, however, it is necessary to consider the possibility of formation of interfering gases. Confirmation of the suspected interfering gases can be made by simple detection methods. Upon identification of the interfering gas(es) the proper packing(s) can be selected to ensure the selectivity of the device. The advantage of the method lies in its inherent simplicity and the possibility of simultaneous measurements (the signal curve of the device can be recorded along with the TG, DTG, and DTA curves).

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Zusammenfassung — Es wird ein geeignetes Gerät zur kontinuierlichen Detektierung von in thermischen Zersetzungsprozessen freigesetztem Kohlenmonoxid beschrieben. Der Detektor kann direkt an eine thermoanalytische Apparatur mit überwachter Gasatmosphäre angeschlossen werden. Das vom Carriergas aufgenommene Kohlenmonoxid wird durch das Gerät geleitet, das einen Hopcalit-Katalysator enthält. In Gegenwart von Sauerstoff wird das Kohlenmonoxid in Kohlendioxid überführt und die durch die Reaktionswärme verursachte Temperaturänderung gemessen. Erfahrungsgemäß ist die Temperaturänderung proportional der entwickelten Menge Kohlenmonoxid.

Das Detektorsignal kann mit den gleichzeitig aufgezeichneten thermoanalytischen Kurven verglichen und zur Bestimmung dessen benutzt werden, in welchem Teilschritt Kohlenmonoxid freigesetzt wird.

Der Detektor zeigt keine vollständige Selektivität, jedoch können Störgase durch verschiedene Füllungen zwischen Thermoanalysator und Detektor vom Carriergas getrennt werden.