AN AUTOMATED EVOLVED GAS DETECTION APPARATUS

L. E. NESBITT* AND W. W. WENDLANDT**

Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)

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ABSTRACT

An automated evolved gas detection apparatus is described consisting of a furnace, furnace temperature programmer, automatic sample changer, thermistor thermal conductivity detector, and a two channel recorder. The samples are automatically introduced into the furnace chamber, pyrolyzed to a preselected temperature limit, and then removed. After the system has cooled to a preselected lower temperature limit, the cycle is repeated. Eight samples can be studied in a sequential manner.

INTRODUCTION

According to the ICTA nomenclature committee recommendations[1], the technique of evolved gas detection (EGD) is defined as the term covering any technique of detecting whether or not a volatile product is formed during thermal analysis. Likewise, the technique of evolved gas analysis (EGA) is a technique of determining the nature and/or the amount of volatile product or products formed during thermal analysis. Both of the EGD and EGA techniques are useful in supplementing data obtained by other thermal analysis techniques such as thermogravimetry (TG) and differential thermal analysis (DTA).

The origin of the EGD technique is subject to some question. Mackenzie[2] suggested that Wedgwood[3,4] founded it on the basis of some rather crude experiments with China-clay. In a very crude experiment, he heated pieces of the clay in a sealed vessel attached to a bladder and then observed its contents. A somewhat more modern viewpoint[5] is that the technique was probably envisioned by Stone[6] in 1952 as a result of his dynamic gas atmosphere, enclosed furnace type of DTA apparatus. Unfortunately, he did not monitor the evolved gases from the furnace chamber. In 1960, Lodding and Hammell[7] placed a thermal conductivity detector at the gas outlets of a DTA furnace assembly but again no evolved gas curves were published. They also

included absorption tubes in the system so that the evolved gases could be analyzed as well as detected.

Rogers et al.[8], also in 1960, described a simple pyrolysis apparatus which was to give birth to this thermal analysis technique. Because of the thoroughness of this investigation, Rogers is generally considered to be the originator of this technique. A year later, Vassallo[9] described a similar apparatus which was used to study the pyrolysis of polymeric materials.

The combination of EGD with other thermal analysis techniques such as DTA, was first described by Ayres and Bens[10] and by Wendlandt[11]. Other simultaneous techniques, also involving EGD and EGA, have been summarized by Wendlandt[12].

The modern evolved gas detection apparatus consists, generally, of a furnace, furnace temperature programmer, a gas detector of some type, and a recorder. It is capable of automatic operation in that after manually inserting the sample, the temperature rise is controlled by the programmer, which will turn off the instrument after a preselected temperature limit is attained. After cooling the furnace back to room temperature, the pyrolyzed sample is removed from the sample holder, a new sample is introduced, and the heating cycle is repeated.

In a continuation of our previous developments of automated DTA[13] and TG[14,15] instrumentation, we wish to report here an automated EGD apparatus which is capable of studying eight samples in a sequential manner. The samples are automatically introduced into the furnace, pyrolyzed to a preselected temperature limit, and then removed. After the furnace has been cooled back to room temperature, the cycle is repeated. Operation of the sample changing mechanism, the furnace temperature rise and cooling, recording, and so on, is completely automatic.

EXPERIMENTAL

EGD apparatus

A block diagram of the automated EGD apparatus is shown in Fig. 1. Basically, the apparatus consists of a sample changing mechanism and furnace, a programmer
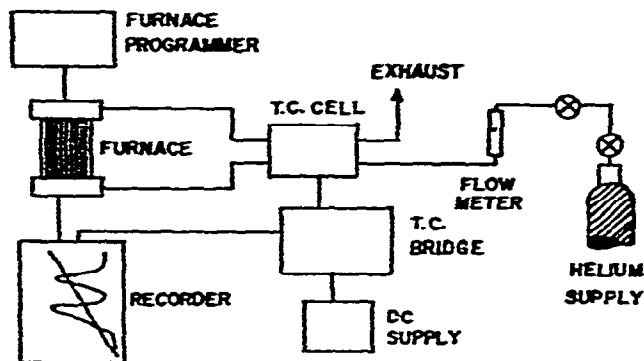

Fig. 1. Block diagram of the automated EGD apparatus.

to control the rate of furnace temperature change, a thermistor thermal conductivity cell and bridge circuit, a two-channel strip-chart potentiometric recorder, and a helium supply and gas flowmeter. Most of the components used were already available in the laboratory. The electronic circuits for the sample changer mechanism were the same as previously described for the automated DTA apparatus[12].

The main component of the EGD apparatus is the sample changer mechanism, which permits the automatic loading and removal of the samples. It is illustrated in Figs. 2–4.

The sample, which is placed in an aluminum cup on a Pyrex rod centered in a sample lift disc, is elevated into the furnace and positioned immediately below a pair of thermocouples. An "O" ring, seated in a groove in the lift disc, seals the furnace so that the carrier gas entering the furnace base continuously circulates through it. The upper limit of travel of the lift disc platform is set by a microswitch which controls the reversible motor driving the platform elevation screw. As the furnace is sealed, the furnace programmer, on a relay delay circuit, is powered. The furnace is a Vycor tube, 25 mm in diameter and 6.4 cm in length, which is wound with 15 Ω of Nichrome II
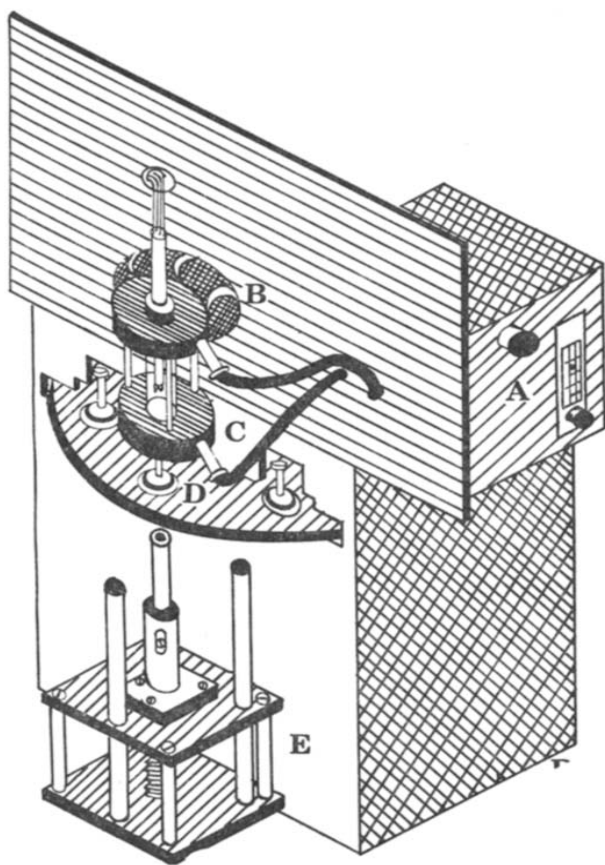
Fig. 2. General view of EGD sample changer mechanism. (A) Gas metering valve and T.C. cell chamber; (B) cooling fan; (C) furnace assembly; (D) lift disc; and (E) platform.

A. THERMOCOUPLES
B. FURNACE TOP

COPPER TUBING

D. VITON "O" RING
E. HEATER WINDINGS
   AND INSULATION ON
   VYCOR TUBING
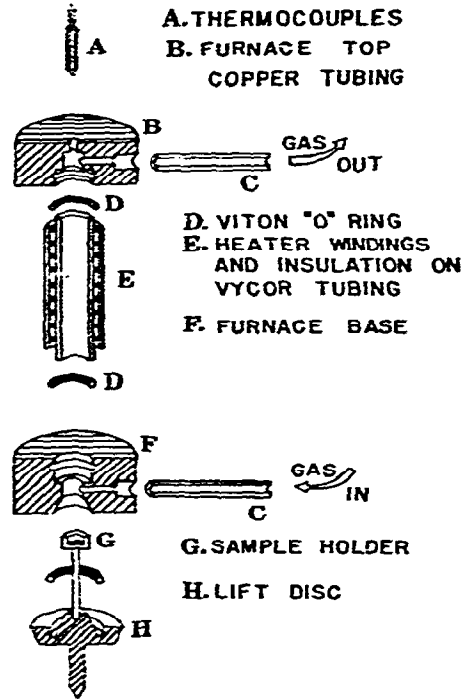
F. FURNACE BASE

G. SAMPLE HOLDER

H. LIFT DISC

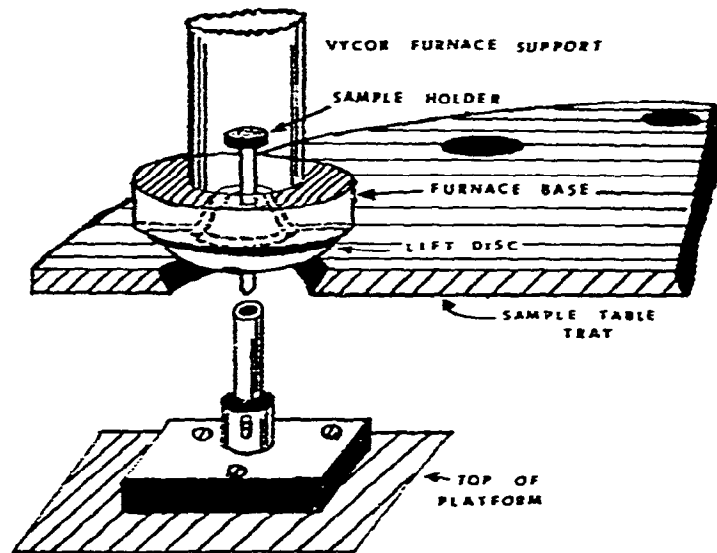Fig. 3. Exploded view of the EGD apparatus sample changer.

Fig. 4. Detailed view of the EGD sample chamber.

resistance wire and covered with suitable asbestos insulation. As the furnace is sealed, the chart drive of the 2-pen (Varian Model G-22) strip-chart recorder is also powered. When the furnace temperature reaches a preselected maximum limit, the sample lift disc is lowered from the furnace and set back into its place on the sample table tray. This tray is rotated by a small synchronous electric motor equipped with an electromagnetic clutch. The rotation of the tray by the motor is controlled by a lamp–slit–photocell arrangement, previously described[13]. As the tray rotates, the furnace programmer is automatically reset, and the cooling fan actuated. When the furnace temperature drops to a preset minimum (normally room temperature), a meter relay controlled by one of the furnace thermocouples starts the next cycle of operations, replicating what has just been described. The cycle is repeated eight times, after which a groove cut into the sample table tray intercepts a roller type microswitch which cuts off all power to the instrument.

The gas flow to the furnace is controlled by a 2-stage gas regulator, a metering valve, and a valved flowmeter. Gas leaving the flowmeter passes first through one port of the thermostatted thermistor type thermal conductivity cell, to the base of the furnace, through the furnace to the other port of the thermal conductivity cell, and then exhausts to the atmosphere. The 2-pen recorder simultaneously records both the furnace temperature and the unbalance of the thermal conductivity cell Wheatstone bridge circuit.

The furnace used here has a temperature range limited by the aluminum sample holders and Pyrex glass rods for the sample supports. In principle, these could easily be substituted by platinum and quartz so that higher temperatures could be employed. Aluminum sample holders, however, have the advantage of being inexpensive and disposable.

Sample sizes ranged in mass from 10 to 40 mg and a gas flow-rate of 50 to 100 ml min^{-1} was normally employed. A furnace heating rate of 2.5 to 10°C min^{-1} was used with a maximum temperature limit of about 300°C.

Procedure

The procedure for a run consists of weighing out the samples into the aluminum sample holders, cementing these to the Pyrex lift disc rods, and placing the lift discs into position on the sample table tray. A gas flow-rate is selected by adjustment of the four valves in the metering system and a bridge balance point, based on the flow-rate is set on the trimmer resistances and the main voltage of the bridge circuit. An upper and lower temperature limit for the furnace temperature are selected on the relay meter. Operation of the instrument is then completely automatic.

RESULTS AND DISCUSSION

Two sequential runs of copper(II) sulfate 5-hydrate are illustrated in Fig. 5.

The EGD curves initially reflect the fact that the system is filled with air which is displaced by the flow of helium gas. It requires about 3 min to purge the apparatus
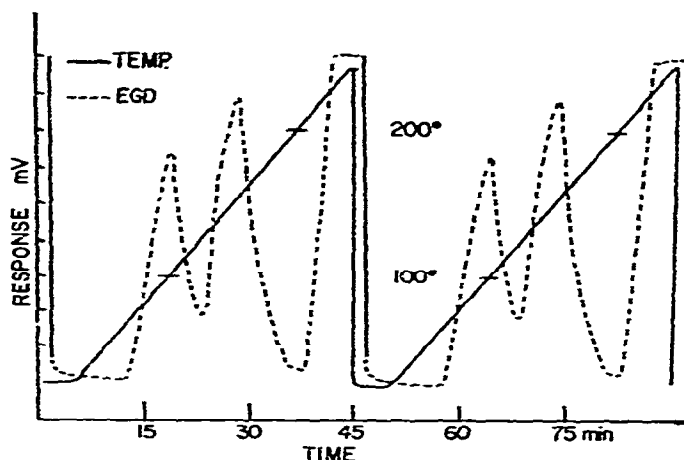
Fig. 5. Two sequential EGD curves of $CuSO_4 \cdot 5H_2O$. Heating rate $10\,^{\circ}C$ min^{-1} at a helium flow-rate of 50 ml min^{-1}.

(flow-rate of 50 ml min^{-1}) of air at the beginning of each cycle. Several more minutes are allowed to permit the EGD curve to establish a level baseline. The samples are then heated linearly to the preselected maximum temperature. Two regions of gas evolution are observed for this compound corresponding to the reactions:

$$CuSO_4 \cdot 5H_2O(s) \rightarrow CuSO_4 \cdot 3H_2O(s) + 2H_2O(g)$$

and

$$CuSO_4 \cdot 3H_2O(s) \rightarrow CuSO_4 \cdot H_2O(s) + 2H_2O(g)$$

These curves are similar to those previously reported[10].

Numerous metal salt hydrates have been studied using the automated EGD technique. As with other EGD instruments, the data obtained are useful for the interpretation of DTA or DSC curves. The technique can be more quantitative if an analytical technique, such as IR, GC, or MS, is coupled to it for analysis of the evolved gaseous products.

The obvious advantage of this apparatus is the automatic changing of the eight samples contained in the sample tray. Operation is completely automated and once begun, does not require the attention of the operator. By the addition of a suitable data-logging system, the apparatus can be made semi-quantitative or even quantitative if carefully calibrated. Also, a small digital computer can be used to control the pyrolysis sequence and other operational parameters.

ACKNOWLEDGMENTS

REFERENCES

1 R. C. Mackenzie, *Talanta*, 16 (1969) 1227.
2 R. C. Mackenzie, *Differential Thermal Analysis*, Vol. 1, Academic Press, London, 1970, p. 18.
3 J. Wedgwood, *Phil. Trans. Roy. Soc., London*, 74 (1784) 358.
4 J. Wedgwood, *Phil. Trans. Roy. Soc., London*, 76 (1786) 390.
5 W. W. Wendlandt, *Thermal Methods of Analysis*, Wiley-Interscience, N.Y., 2nd ed., 1974, Ch. 9.
6 R. L. Stone, *J. Amer. Ceram. Soc.*, 35 (1952) 76.
7 W. Lodding and L. Hammell, *Anal. Chem.*, 32 (1960) 657.
8 R. N. Rogers, S. K. Yasuda and J. Zinn, *Anal. Chem.*, 32 (1960) 672.
9 O. A. Vassallo, *Anal. Chem.*, 33 (1961) 1823.
10 W. M. Ayres and E. M. Bens, *Anal. Chem.*, 33 (1961) 568.
11 W. W. Wendlandt, *Anal. Chim. Acta*, 27 (1962) 309.
13 W. W. Wendlandt and W. S. Bradley, *Anal. Chim. Acta*, 52 (1970) 397.
14 W. S. Bradley and W. W. Wendlandt, *Anal. Chem.*, 43 (1971) 223.
15 W. W. Wendlandt, *Chimia*, 26 (1972) 1.