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EMISSION THERMOPHOTOMETRY. AN IMPROVED APPARATUS

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ABSTRACT

An improved emission thermophotometry (ETP) apparatus is described. The apparatus consists of a furnace and sample holder, a temperature programmer, a 1P28 PMT and photometer, and a microcomputer data collection system. Use of the apparatus is illustrated by the ETP curve of ethyl cellulose.

INTRODUCTION

The light emission (LE) of polymers, organic compounds, coordination compounds, and many other substances has been of interest in this laboratory since 1976. For lack of a better name, the term "light emission" (LE), was employed to describe this technique although Ashby [1] called it "oxyluminescence" in his applications to polymers. Barker et al. [2] used the term "thermochemilumescence" while David [3] called it "photothermal analysis" (PTA). Because of the broader application of this technique to substances such as coordination compounds, this laboratory has preferred the name "light emission". From the viewpoint of the nomenclature proposed by the International Confederation for Thermal Analysis (ICTA) [4], a more appropriate name is emission thermophotometry (ETP) since the technique measures the emission of light from a sample as it is heated in an air or oxygen atmosphere at a controlled temperature program (i.e., increasing heating rate). The ICTA defines the thermal analysis technique of "thermophotometry" as the measurement of total light; the adjective "emission" would make the name more definitive.

This paper aims to describe another apparatus for the measurement of emission thermophotometry that has numerous improvements over previous systems used in this laboratory. Wynne and Wendlandt [5], described a system based on a photon counter attached to a DSC apparatus. For another apparatus, Wendlandt [6] described a controlled atmosphere sample holder and furnace capable of operation at reduced pressures from 10–760 torr. A 1P28 photomultiplier tube (PMT) and photometer were used to measure the

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light emission of the sample. This apparatus was later modified to permit simultaneous LE–DTA measurements [7] and hence, application to coordination compounds containing reducing and oxidizing ligands.

The apparatus described here is based on a similar PMT and photometer. The PMT is part of the enclosure for a DSC cell which is attached to a commercial Omnitherm thermal analysis system. A microcomputer data collection and display system are used to record and store the photometer and thermocouple outputs so that plots of light emission versus temperature can be made. These plotted data are called emission thermophotometric curves and contrary to previous systems [8], do not require a correction for the PMT background emission.

EXPERIMENTAL

Apparatus

A schematic diagram of the apparatus is shown in Fig. 1, while the furnace and sample holder are illustrated schematically in Fig. 2.

The apparatus consisted of the following components: (a) an Omnitherm thermal analysis controller which contained the temperature programmer and temperature measurements circuitry; (b) a DSC furnace and sample holder enclosure containing the PMT; (c) a photometer (American Instrument Co., Silver Spring, MD); (d) a four-channel differential amplifier (Bascom-Turner, Model 104, Newton, MA); (e) two Keithley Model 177 digital microvolt multimeters (DMM) to monitor the voltage outputs from the photometer and Omnitherm controller; (f) an Apple Model IIe microcomputer equipped with a Dynamic Solutions Is11 16 channel, 12 bit, analog-to-digital converter and using Dynamic Solutions Corp. (Pasadena, CA) Appligration II software; and (g) an Epson Model RX-80 dot matrix printer.

The sample holder was constructed from a DuPont DSC cell by removing

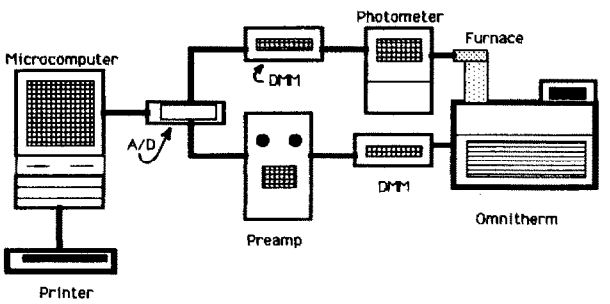

Fig. 1. Schematic diagram of the emission thermophotometry apparatus.

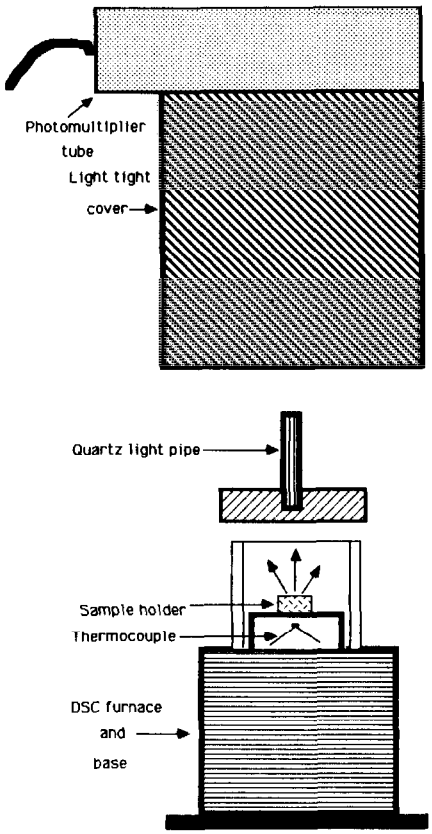

Fig. 2. Schematic diagram of the furnace and sample holder of the ETP apparatus.

the thermoelectric disk element and substituting for it a platform made from a thin nickel metal sheet. The sample, contained in a 7.0-mm diameter aluminum container, was positioned in the center of the Ni platform. An enclosure, made from a machined aluminum cylinder, covered the DSC cell and quartz rod light pipe (8×50 mm). The latter covered the top of the furnace preventing or reducing thermal atmosphere gradients in the sample chamber. The light-tight enclosure covered the entire sample and furnace chamber. The 1P28 PMT, encased in a metal cylinder, was attached to the sealed end of the enclosure; it contained a 1-cm diameter opening located just above the quartz light pipe. Any light emitted by the sample in the furnace chamber was thus transmitted to and detected by the PMT. All inside surfaces of the metal enclosure were painted black to reduce internal reflections.

Procedure

The procedure for obtaining an ETP curve was essentially identical to that previously described [8]. The sample (5–10 mg) was weighed out into the

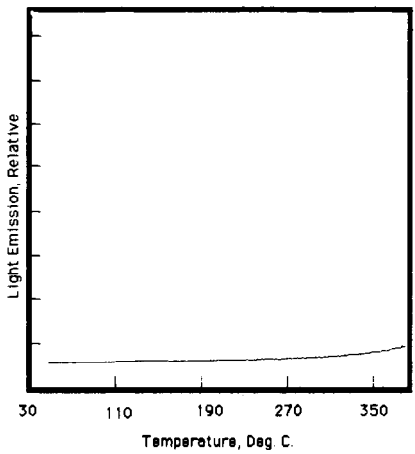

Fig. 3. Background ETP curve of the ETP apparatus. Heating rate of 20°C min^{-1} in oxygen.

aluminum container and positioned in the furnace chamber. After assembly, the furnace chamber was flushed with oxygen, maintaining an oxygen flow rate of about 40 ml min^{-1} during the run. A furnace heating rate of 20°C min^{-1} was normally used, but it could be varied from 0 to 50°C min^{-1}. Photometric and temperature data were collected by the microcomputer system and stored on 5.25-in. floppy disks. After collection and storage of the data, the ETP curves were printed out on the dot matrix printer using various X–Y scale coordinates.

RESULTS AND DISCUSSION

The background ETP curve, without a sample in the furnace chamber, is shown in Fig. 3. As can be seen, the light emission is very low compared to the previous apparatus [8] and did not require a correction in the ETP sample curves. Apparently, the furnace and light pipe enclosure keeps the thermal and radiative emissions at negligible levels; hence, the background emission of the PMT is quite low in the temperature range from 30 to 400°C. The heating rate, as ascertained from a temperature–time curve, appeared to be linear with time to within $\pm 5\%$. To illustrate the use of the apparatus, an ETP curve of ethyl cellulose is shown in Fig. 4. The curve is expanded on the light emission axis 1.5 times. Light emission from the sample began at about 150°C and culminated with a peak maximum at 250°C. Most of the ETP activity with numerous other materials that were examined occurred in the 200–400°C temperature range. As discussed previously [9], the origin of the

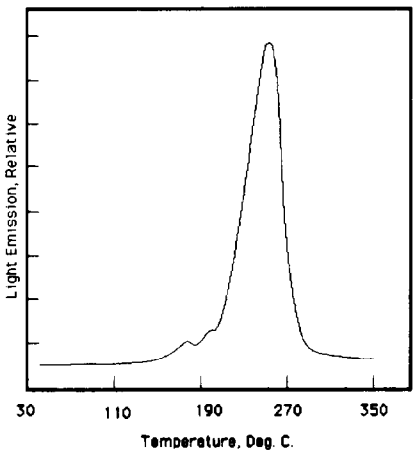

Fig. 4. ETP curve of ethyl cellulose. Heating rate of 20°C min^{-1} in oxygen.

light emission process is probably a surface oxidation phenomenon, the mechanism of which is still not known.

ACKNOWLEDGMENT

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