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COMPOSITIONAL ANALYSIS BY COUPLED THERMOGRAVIMETRY–COLORIMETRIC TITRATION *

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ABSTRACT

Compositional analysis of materials can frequently be made by the determination of a selected substance formed by thermal degradation. This presentation describes a coupled thermogravimetry–colorimetric titration technique for such an application. Thermogravimetry serves not only to decompose the sample under controlled conditions to release the substance to be analyzed, but also provides mass-change information and prior separation of undesirable materials. A microprocessor-controlled titrator equipped with a dipping probe colorimeter is then programmed to perform the titration automatically, calculate the results, and print out the analytical report. This technique should be potentially useful in cases where traditional chemical or spectroscopic methods are time-consuming or encounter interferences. Examples of using this technique for the determination of copolymer compositions are shown.

INTRODUCTION

Thermogravimetry (TG) is most widely used for studying the thermal stability and decomposition of a large variety of materials. Based on differences in thermal stability and volatility of the various components in a sample, compositional analysis can frequently be made using thermogravimetry, especially with proper manipulation of the temperature program and gaseous environment. Proximate analysis of coal and additives determination in reinforced plastics are good examples. Copolymer compositions can also be determined by thermogravimetry if a well-defined weight-loss step is quantitatively related to a comonomer. However, more often than not, this weight-loss step is complicated by the presence of other volatiles or overlapping adjacent weight losses. To remedy this situation, thermogravimetry is combined with potentiometric titration to allow selective determination of the component of interest and disregard the others [1]. The present work

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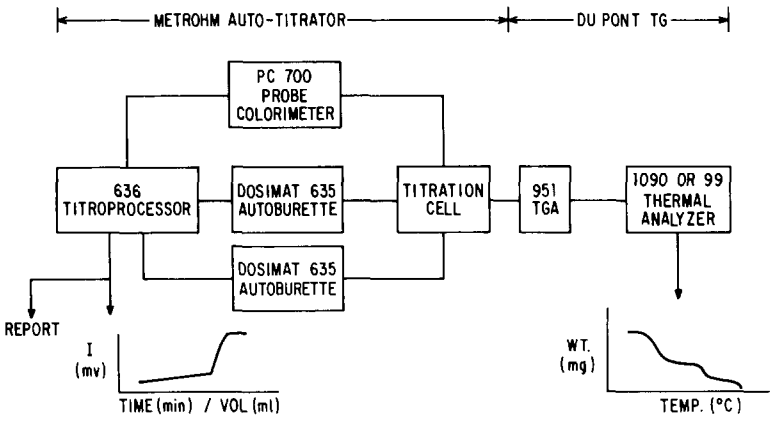

Fig. 1. Schematic diagram of combined TG–colorimetric titration system.

further extends this technique to sample systems where released volatiles cause fouling of the sensing electrodes. The electrodes are now replaced by a dipping probe colorimeter, and the titration end point is indicated by a color change.

The combined thermogravimetry–colorimetric titration technique is illustrated by the determination of the composition of ethylene–vinyl acetate (E/VAc) copolymers and emulsions of partially hydrolyzed polyvinyl acetate (PVAc). The analysis of the former is easily performed by potentiometric titration of acetic acid released from the thermogravimetric analyzer as shown previously [1], but evolution of volatiles other than acetic acid causes electrode fouling which requires cleaning after each run, such as in the case of the emulsions. This problem is avoided with the colorimetric method.

EXPERIMENTAL

A schematic diagram of the apparatus is shown in Fig. 1. A DuPont 951 thermogravimetric analyzer module controlled by either a DuPont 1090 or 99 programmer is coupled to a Metrohm auto-titrator. The DuPont 951 and 1090 are used in the standard fashion to obtain weight loss as a function of temperature. Typical sample weights are in the range 10–100 mg. A heating rate of 10°C min^{-1} and a nitrogen flow of 100 ml min^{-1} are maintained. The microprocessor-operated Metrohm Titroprocessor E636 controls two Dosimat E635 autoburettes for adding two types of reagents. The end point is indicated by the PC 700 probe colorimeter.

The TG effluent is swept into the titration cell through a delivery tip made of quartz tube with a female 12/5 spherical ground joint connected to the TG furnace tube end as shown in Fig. 2. The size of the capillary tip is

important for good recovery of the desired component, and we have found an inside diameter of 1.6 mm (1/16 in.) or smaller to be satisfactory.

The titration cell is schematically shown in Fig. 3. It contains the sample delivery tip, the probe colorimeter, and two reagent burette tips. The burette has a specially designed antidiffusion tip to reduce back diffusion to the nanoliter range. The operational schematic for the Brinkmann probe colorimeter is shown in Fig. 4. It utilizes one-half of the fiber optic bundles to transmit the phase-shifted, AC modulated light into the sample solution, and the other half to return the light to the instrument where it passes through an interference filter (600 nm in the present work) prior to impinging on a silicon detector cell. The effective path length of the light in the solution is twice the distance between the mirror and the end of the fiber optics.

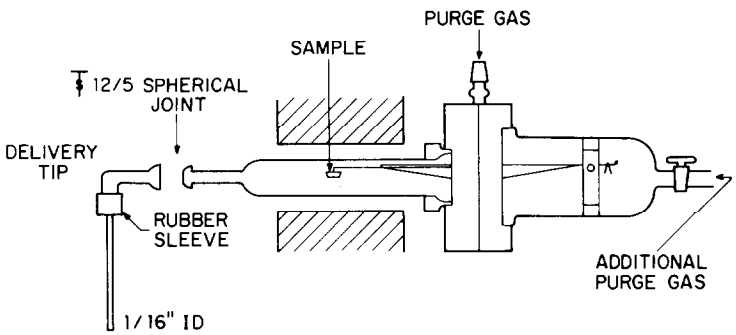

Fig. 2. Interfacing TG with titration.

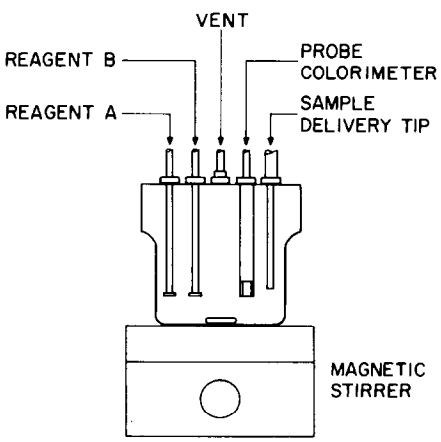

Fig. 3. Schematic diagram of the titration cell.

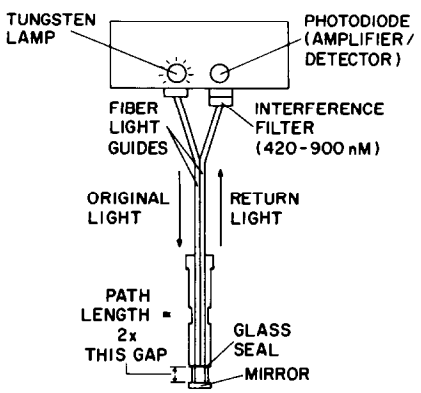

Fig. 4. Schematic diagram of the Brinkmann probe colorimeter.

RESULTS AND DISCUSSION

Typical TG scans are shown in Fig. 5 for an ethylene–vinyl acetate copolymer sample and an emulsion sample of partially hydrolyzed polyvinyl acetate, respectively. Ethylene–vinyl acetate copolymers produce acetic acid in the first major weight-loss step in the temperature range 260–380°C, which is stoichiometrically related to the vinyl acetate content. The off-gases can be led into the titration cell at the beginning of the run until well beyond this weight loss step. In the case of the emulsion samples, the TG scan is used as a guide for initial separation of most of the undesired volatiles including methanol, acetic acid, vinyl acetate monomer, water, etc., and a "dry" sample weight is obtained from a plateau in the vicinity of 200°C. The next weight loss step, occurring at 220–340°C, then releases the acetic acid for compositional analysis. However, complete removal of the early volatiles is not essential in the colorimetric method.

The TG effluence is absorbed in 20 ml of aqueous 0.005 N NaOH solution which is dispersed into the titration cell by one autoburette, then 10 drops of aqueous 0.04% (w/w) bromthymol blue solution are added to serve as the colorimetric indicator of choice in this pH range. The unreacted blue caustic solution is then back-titrated with 0.005 N HCl solution automati-

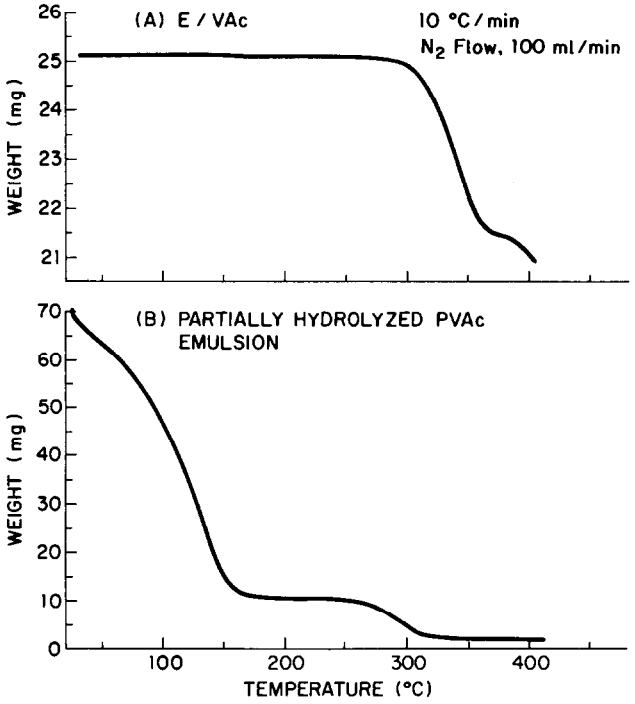

Fig. 5. TG scans of VAc copolymers.

TABLE 1

Compositional analysis by thermogravimetry–colorimetric titration

Sample	Description	Mol% VAc	
		Nominal	Determined
HOAc	1 ml 0.03 N solution	1.8 (mg)	1.8, 1.8, 1.9
	3 ml 0.03 N solution	5.4 (mg)	5.5
E/VAc	ASTM Round Robin	7.4	7.8, 7.5
Partially hydrolyzed PVAc	Experimental emulsion	7.5	6.5, 6.2
		10	11.8, 8.7, 7.7
		12	15.8, 15.6
		14	11.8, 11.7, 10.9
		16	14.4, 15.2
		23	27.1, 24.0, 25.3

cally from the other autoburette. The end point is detected by the probe colorimeter when the indicator turns yellow. The titroprocessor is programmed to automatically add the absorbing solution, perform the titration, calculate the results, and print out the analytical report.

We have tested hundreds of samples by this procedure with very good results. For example, when a sample of ethylene–vinyl acetate copolymer with 20% vinyl acetate is repeatedly analyzed, results are within 0.2% of the vinyl acetate values obtained by the time-consuming saponification procedure. Table 1 shows some selected data including standards and actual samples. It is noted that the capability of the technique is limited by uniform sampling of the emulsions rather than by the precision of the method.

CONCLUSIONS

We have demonstrated another one of a family of techniques combining thermogravimetry with automatic titration, this one based on colorimetry. It complements the potentiometric and ion-selective electrode titrations previously described, and should enhance the overall capability of thermogravimetry as a tool for compositional analysis.

REFERENCE

1 S.G. Fischer and J. Chiu, Thermochim. Acta, 65 (1983) 9.