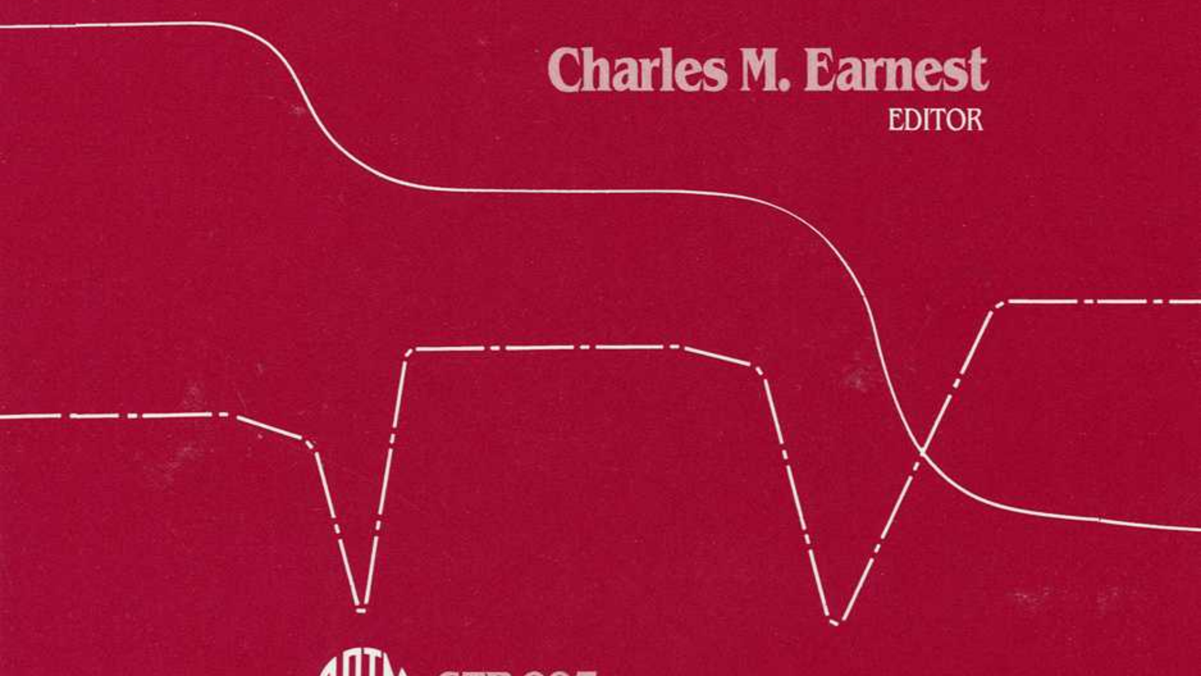
Compositional Analysis by Thermogravimetry



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Foreword

The Symposium on Compositional Analysis by Thermogravimetry was presented in Philadelphia, PA, 16–17 March 1987. The symposium was sponsored by ASTM Committee E-37 on Thermal Measurements. Charles M. Earnest, Berry College, served as chairman of the symposium and is editor of the resulting publication.

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Compositional Analysis Using Hyphenated TG Techniques and New Instrumental Concepts

Compositional Analysis of Inorganics, Fuels, Minerals, and Raw Materials

Overview

The Special Technical Publication is the result of an international symposium, which was held 16 and 17 March 1987 at Philadelphia, PA. This symposium was organized and sponsored by the ASTM Committee E-37 on Thermal Measurements. The symposium as well as the special technical publication cover a broad spectrum of applications of thermogravimetry to the compositional analysis of materials. We are very pleased with the wide range of material types (polymers, rubber, cements, coal, oil shales, clays, and so forth) as well as the fact that authors from seven different countries participated in this symposium and subsequent publication.

This symposium was held as one of the activities of Subcommittee E-37.04 on Technical Programs, which is just one of many such active subcommittees and task groups that operate under the jurisdiction of Committee E-37 on Thermal Measurements. The symposium was organized and chaired by C. M. Earnest (Berry College, Rome, GA) who also served as chairman of Subcommittee E-37.04 on Technical Programs at the time.

In his welcoming remarks at the symposium, C. M. Earnest indicated that to many of the ASTM E-37 committee members the event was being held as a celebration. He went on to explain that the ASTM document "Test Method for Compositional Analysis By Thermogravimetry" had been completed by the committee and that the test method had successfully passed all levels of ASTM balloting. Thus, ASTM Committee E-37 had generated another standard for use by practicing thermal analysts. This document has been assigned an ASTM method number of E 1131.

Danny Larkin (Detroit-Diesel Allison, Detroit, MI) served as chairman of the task group that generated this procedure for thermogravimetric (TG) compositional analysis. Larkin has written a paper entitled "Compositional Analysis: The Development of a Standard Method." This paper is included in this book (STP 997) and describes the development of the document, round-robin studies, and the final recommended standard practice for performing compositional analysis by modern thermogravimetry for a variety of materials.

Earnest in his welcoming remarks also described the symposium as an historic event. He pointed out that it had been more than 30 years since the visit of the French scientist Clement Duval to this country. Duval came to promote the technique of thermogravimetry, which had been slow coming into use in the United States. Duval gave seminars in Washington, DC and Baton Rouge, LA. Most of Duval's presentations dealt with the thermogravimetric characterization of more than 1000 analytical precipitates, which he had organized into a book.

Earnest said that this symposium on "Compositional Analysis By Thermogravimetry" is an historic occasion since at no time in history has an international group of scientists gathered together for two entire days to discuss one application area (that is, compositional analysis) of thermogravimetry. "This is indeed a historic moment in the development and maturation of the technique of thermogravimetry," he said. He also stated that the application of TG to the compositional analysis of materials represents what is probably the most analytical of all thermogravimetric procedures. The results are generally presented in weight percent of the original sample material. Earnest went on to say that if all TG applications were as analytical as the compositional analysis applications, no nomenclature committee would have ever removed the "A" from "TGA".

Thermogravimetry (TG) is a technique in which the mass of a substance is continuously monitored as a function of temperature (or time) as the substance is subjected to a controlled temperature program. Thus, the data obtained from the TG experiment are displayed as a thermal curve with an ordinate display having units of weight (or weight percent) and the abscissa may be in units of either temperature or time. Many types of materials can be characterized by the techniques of thermogravimetry. This publication serves as a testament of this fact.

Some applications of thermogravimetry only involve the assignment of either the thermal stability of a material or the oxidative stability (in an oxidizing atmosphere) as the material is subjected to a controlled heating program. These applications involve a temperature assignment for the corresponding decomposition or oxidation. Such assignments are often referred to as "thermal testing" or "thermal measurements" rather than "thermal analysis".

On the other hand, there are a number of applications of thermogravimetry that characterize materials by the quantitative weight losses that occur in specified temperature regions of the TG thermal curve. In most TG studies the mass loss is read directly by modern day instrumentation in units of weight percent of the original sample quantity. This type of application may be referred to, in many cases, as "compositional analysis" and is the subject of this entire book.

Compositional analysis as described here is taken in its broadest sense to mean any analysis whose results produce information relating to the composition of the material. Within this loose definition, we find two types of analytical assignments when using thermogravimetry. The first of these includes those weight loss events in which the absolute weight loss observed over a specified temperature range is reported as the analytical value for the thermal event. A common example of this is the assignment of moisture content of polymers and coals. Another example would be the determination of residual solvent in many pharmaceutical compounds. The determination of ash value or ash residues also fall into this category since the remaining weight is read directly as weight or weight percent.

In the second type of TG compositional analysis the measured weight loss for the thermal event is multiplied by a gravimetric factor in order to assign the percentage of the component in the original sample material. The use of the gravimetric factor for such assignments is discussed in the first chapter of this publication by Earnest. He specifically demonstrates the use of the gravimetric factor for the determination of calcium carbonate, which is a common filler used in organic polymers. In this case, the decomposition of the assigned component must be stoichiometrically defined and a balanced chemical equation must be known for the weight loss event.

Several authors include the determination of calcium carbonate content of materials in these papers included in this technical publication. Seyler and Gillmor use the gravimetric factor to assign the calcium carbonate content of the ash from a polystyrene, carbon black, calcium carbonate, iron oxide system. Likewise, Dorsey and Buecker use the TG weight loss assignment to determine the calcium carbonate content of limestones.

In his paper entitled "Determination of the Degree of Mixing of Sheet Molding Compound Paste Using the Thermogravimetric Method," Hua-Tie Kau of the General Motors Research Laboratories used the TG technique and gravimetric factor to assign the calcium carbonate filler in sheet molding compound (SMC) formulation. Likewise, the calcium carbonate filler was assigned by P. J. Lorigan Allen in similar SMC compound formulations.

Culmo and Fyans describe the determination of the residual calcium carbonate in a fluidized bed coal combustion process by thermogravimetry. They also uniquely regenerate calcium carbonate from the calcium oxide and by comparison determine the degree of utilization in the removal of sulfur oxides from the combustion furnace.

All of the so called "proximate analysis" procedures by either classical gravimetry or by modern thermogravimetry belong to the first category of TG compositional analysis, which was described above. The proximate analysis of coals and coal derived materials using modern thermogravimetry has become widely practiced by coal users primarily because of the speed of the analysis. In this case, one coal specimen may be analyzed for percentage moisture, total volatiles, fixed carbon, and ash residue in less than 30 min. It has been the coal users (power plants, coal burning industries, and so forth) that have adapted the rapid thermogravimetric method, not the coal vendors. The coal companies (vendors) have stayed with ASTM Committee D-5 gravimetric procedures for proximate analysis (ASTM Method for Proximate Analysis of Coal and Coke [D 3172]). The rapid TG proximate analysis of coals is described in three chapters of this book. Charsley and Warrington use the rapid TG proximate analysis of coals as one of their examples in their paper entitled "Industrial Applications of Compositional Analysis by Thermogravimetry." A more detailed discussion of the TG proximate analysis of coals (as well as other fillers) is presented in a later chapter of this publication (STP 997) by Agrawal in his paper "Compositional Analysis of Solid Waste and Refuse Derived Fuels by Thermogravimetry." Wiedemann and Riesen describe the use of the proximate analysis procedure to study a variety of materials representing different types and varying degrees of carbonized wood. These include California redwood, peat moss, soft coal, bituminous coals, and anthracitic coals.

The proximate analysis of coals and fuels is not by any means the most commonly practiced compositional analysis procedure performed by modern thermogravimetry. The compositional analysis of elastomers is a very similar procedure to that used in coals. The compositional analysis of elastomers is well represented in this book. Sacher, Macaione, and Singer describe herein an extensive program that was executed at the U.S. Army Materials Technology Laboratory in Watertown, MA. In this program more than 50 different carbon filled elastomeric compounds were analyzed by thermogravimetry to document the percent volatiles, organics, carbon black, and inorganic residue.

Earnest also describes the compositional analysis of a rubber specimen tire by thermogravimetry using a multi-step heating program with purge gas switching from inert to oxidizing atmosphere to burn off the carbon black and assign the residual inorganic ash. A generalized procedure with guidelines for executing such programs for carbon filled elastomers and polymers is included in the paper by Larkin. This chapter discusses the recommended methodology for performing TG compositional analysis that was developed by ASTM Committee E-37.

Advances in the development of modern computerized equipment have automated many of the compositional analysis procedures by thermogravimetry. This is primarily due to the advent of microcomputer-based controllers (temperature programmers) as well as microcomputer data handling devices. The computerization of the thermogravimetric technique is discussed in this book by Earnest in the first chapter entitled "The Modern Thermogravimetric Approach to the Compositional Analysis of Materials."

One complete section of this special technical publication is devoted to "Compositional Analysis Using Hyphenated TG Techniques and New Instrumental Concepts." This portion of the book contains four unique papers. The first of these is by Dyszel (U.S. Customs Service, Washington, DC) who has successfully interfaced her thermobalance to an atmospheric pressure chemical ionization mass spectrometer. The addition of the mass spectrometer to the TG effluent provides qualitative and quantitative information about the composition of the decomposition products. In the second paper Khorami et al. (University of Sherbrooke, Quebec) demonstrate the usefulness of Fourier transform infrared spectroscopy to the analysis of both gaseous decomposition products and condensed liquids obtained from the TG effluent.

De Vos et al. (Shell Research Laboratories, Amsterdam) have included a contribution to this publication. In their work a multi-element evolved gas technique is described using both pyrolysis and combustion techniques followed by quadruple mass spectrometric analysis of the evolved gases. The ash residue from each individual analysis was also recovered and weighed manually. De Vos reports the use of this noncommercial instrument for the analysis of coals, oil shale, heavy oil products, and polymers. Emmerick et al. report the design and performance of a new symmetrical thermomicrobalance. This instrument utilizes dual microfurnaces for both sample and reference pans of the thermobalance. This reduces buoyancy effects to such an extent that very small samples may be analyzed by the technique of thermogravimetry.

The final section of this book is a group of papers dealing with the compositional analysis of fuels, inorganics, minerals, and raw materials. Many of these papers have been mentioned earlier in this overview. This section of the material includes an excellent application of thermogravimetry to the determination of portlandite $Ca(OH)_2$, in portland cement by Dollimore et al. (University of Toledo, OH). Harris (University of Louisville, KY) demonstrates the use of modern thermogravimetry as a diagnostic aid in the retorting of oil shales from Kentucky. This section of the publication also includes an extensive paper entitled "Thermoanalytical Studies on Simple and Mixed Lanthanide Complexes" by Rao of the Visvesvaraya Regional College of Engineering, Nagpur, India. In this work Rao probes the dehydration stoichiometry and decomposition mechanism of several lanthanide coordination complex systems. This is probably the most fundamental research of all the papers included in this book. The last section of the book is concluded with a second paper by Earnest. This paper demonstrates the characterization of selected clays and clay products by thermogravimetry.

Throughout the broad range of applications of thermogravimetry, which is described in this book, there exists two unique papers that have not been mentioned to any extent in the above discussion. One describes the use of TG and TG-mass spectrometry for the compositional analysis of drugs and injectable biological products. This paper was contributed by May et al. of the U.S. Food and Drug Administration, Center for Drugs and Biologics, Bethesda, MD. Published papers on this subject are indeed rare. In another interesting paper, Seyler and Gillmor (Eastman Kodak, Rochester, NY) show how one's knowledge of the chemistry of both the analytical specimen and its associated decomposition products can help one choose the proper, and sometimes innovative, purge gas composition for performing compositional analysis by thermogravimetry.

The accumulation of these 22 papers provides a valuable reference book on the subject of compositional analysis by thermogravimetry. It is in itself just one indication of the continued growth in the use of a rapid, sophisticated, and yet simple technique for the compositional analysis of many materials.

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