Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THERMOGRAVIMETRIC-QUADRUPOLE MASS-SPECTROMETRIC ANALYSIS OF GEOCHEMICAL SAMPLES

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(Received November 24th, 1971)

ABSTRACT

Thermogravimetric-quadrupole mass-spectrometric-analysis techniques can be used to study a wide variety of problems involving decomposition processes and identification of released volatile components. A recording vacuum thermoanalyzer has been coupled with a quadrupole mass spectrometer. The rapid scan capabilities of the quadrupole mass spectrometer are used to identify the gaseous components released. The capability of the thermogravimetric-quadrupole mass spectrometer to provide analytical data for identification of the released volatile components, for determination of their sequence of release and for correlation of thermal-decomposition studies is illustrated by an analysis of the Orgueil carbonaceous chondrite.

INTRODUCTION

Thermal analysis of geochemical samples has yielded valuable information concerning the decomposition processes and phase changes as functions of sample temperature; however, very little work has been carried out on the identification of the volatile components released from these samples during the heating process. The mass spectrometer has been shown to be a powerful tool for monitoring released gases and for determining the identity of species released from a variety of systems[1,2]. Previous instrumentation generally has involved the use of a time-of-flight mass spectrometer connected to the thermal-analysis equipment[2-4]. The problems associated with the use of a time-of-flight mass spectrometer are numerous (*e.g.*, heated gas-inlet lines between the thermal-analysis instrument and the mass spectrometer), and the high cost of the time-of-flight mass spectrometer prohibits most users[5,6]. The recent development of the comparatively inexpensive quadrupole mass spectrometer permits its use in thermal-analysis studies[7]. Analyses with the quadrupole mass spectrometer are rapid; and, because the mass spectrometer source can be installed near the thermal-analysis furnace, continuous monitoring of the release of volatile components in a dynamic system is possible.

In our laboratory, a Mettler recording vacuum thermoanalyzer has been coupled with a Finnigan 1015 quadrupole mass spectrometer. This combination makes thermal analysis an even more powerful tool for the study of thermal degradation and decomposition as well as for routine analytical techniques.

The combination of the thermoanalyzer with the quadrupole mass spectrometer allows the use of a high vacuum, by which the decomposition atmosphere can be controlled and a reproducible working environment for sample study can be achieved. By locating the quadrupole mass-spectrometer ionizer directly in the thermoanalyzer, no time delays are involved in the analysis of the released volatile components. No condensation problems (usually resulting from either water or organic solvents) are encountered, unlike previous methods for which the mass spectrometer is located in a remote position that requires the passage of the evolved gases some distance before analysis[8]. The evolved gases are pumped away from the sample chamber to the quadrupole mass-spectrometer analyzer; therefore, these gases are not allowed to react with the sample under study.

The application of the technique of thermogravimetric-quadrupole mass-spectrometric analysis to geochemical samples permits the complete identification and characterization of the decomposition products. This technique allows the simultaneous recording of the sample-weight change in two sensitivity ranges, recording of enthalpy changes (by using a differential-thermal-analysis sampleholder), recording of pressure changes, performance of kinetic and rate studies of the decomposition processes (through the derivative of the weight-loss curves), and continuous monitoring of the furnace and sample temperature (by using thermocouples). The combination of the thermograms and plots of gas evolution as a function of temperatures gives a complete characterization of the samples. One important aspect of this approach is that only a very small sample is required for the complete simultaneous study.

The application of this technique to the study of the volatile-rich Orgueil carbonaceous chondrite meteorite will be shown. The gas-evolution patterns obtained are correlated directly with the mineralogy of the meteorite.

EXPERIMENTAL

Instrumentation. — The thermal-analysis instrument used in this study was the Mettler recording vacuum thermoanalyzer. This instrument, which has been described previously by Wiedemann[9], is capable of operating at temperatures from room temperature to 1600°C with the sample under a vacuum of 2×10^{-6} torr. Temperatures are programable from isothermal conditions to heating rates up to 25°C/min. During the present study, the samples were heated at 4°C/min. Samples, consisting of 20–30 mg of powdered carbonaceous chondrite meteorite, were weighed directly into 8-millimeter-diameter platinum, dish-type sampleholders. The flat sampleholders allowed the exposure of a large sample surface area with an overall sample thickness of less than 1 mm. Therefore, with this arrangement, problems of diffusion of the evolved gaseous species were minimized. Because the evolved volatile components were pumped away, reaction with the sample was prevented. The sample weights were recorded continuously during the evacuation procedure by the balance of the thermal analyser. This technique allowed a study of adsorbed gaseous species to be made.

The vacuum system of the Mettler vacuum recording thermoanalyzer was modified slightly for this study. One 60-l/sec oil-diffusion pump was replaced by a 260-l/sec oil-diffusion pump and baffle. This modification ensured a greater pumping capacity and, ultimately, achievement of a higher operating vacuum at 2×10^{-6} torr. Evacuation was continued until constant sample weight was achieved before sample analysis was started.

A Finnigan 1015 quadrupole mass spectrometer, which consisted of a mass analyzer and an electronic control console, was used in this investigation. The analyzer of the quadrupole mass spectrometer was coupled to the thermoanalyzer directly by using a stainless steel collar. Crushable 6-inch copper seals were used between the mass analyzer and the collar. Baking of the interface at 250°C by using heating tapes allows bakeout of the mass-spectrometer head and prevents condensation of volatile components around the analyzer during analysis. A schematic of the integrated instruments is shown in Fig. 1.

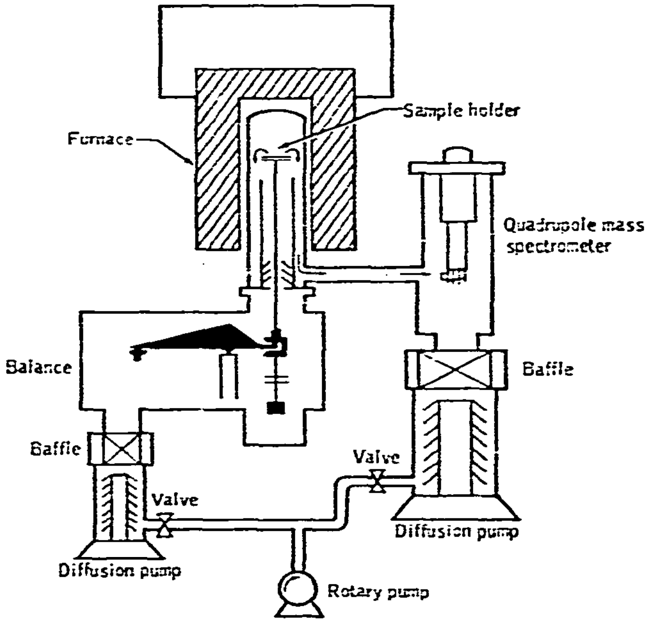

Fig. 1. Schematic of thermoanalyzer-quadrupole mass spectrometer.

The mass spectrometer consists of an ionizer (located 8 in. from the bottom of the furnace), a quadrupole mass filter, and an electron multiplier. Rhenium filaments are used for ionization, and an ionization energy of 70 eV is employed. The positive ions are accelerated from the ion source and injected into the quadrupole mass filter, where they are separated according to their mass. Because no magnetic fields are involved in the ion-separation process, the mass scanning is extremely rapid. This allows for increased sensitivity and detection of volatile species, all at a fast scanning speed. Therefore, the quadrupole mass spectrometer is a powerful tool for examining the rapidly changing gaseous composition of decomposition-reaction products.

The desirable characteristic of the quadrupole, as an ion-sorting device, that enhances its basic sensitivity (as compared with magnetic analyzers) is its capability for accepting the filtering ions over a relatively large inlet-energy spread and at varying entrance angles. This characteristic is well suited for use in the application described herein. In addition, the quadrupole mass filter does not require fine slits at either its entrance or exit in order to accomplish filtering of ions.

After the ions have passed through the mass filter, they are detected by an electron multiplier. The signal from the multiplier then is passed into a preamplifier and displayed on an oscilloscope, a recording oscillograph, or a conventional pen and ink strip-chart recorder. A typical mass spectrum of the background and sample analysis is presented in Fig. 2.

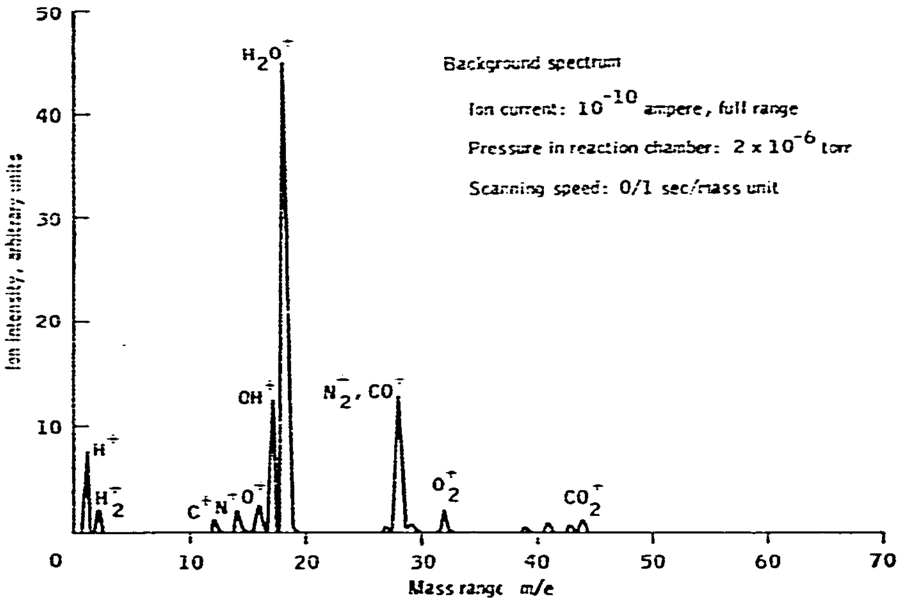

Fig. 2. Typical background spectrum of reaction chamber.

The quadrupole mass spectrometer used in this investigation has three mass ranges: 1–100, 10–250, and 50–750 *m/e*. It is possible to monitor a single mass number only or to scan linearly the entire mass range (or any part of the range) at different scanning rates. Calibrated scan rates of from 0.01 to 1000 sec/mass-unit range or any sub-interval are possible with the variable vernier. The resolution of the instrument is 1000 as mass 500, based upon $m/\Delta m$ when Δm is measured at the half height of the peak.

Procedure. — For simultaneous thermogravimetric-quadrupole mass-spectrometric-analysis investigations in a high vacuum, a definite sample size should not be exceeded. This size is calculated according to the rate of gas evolution during decomposition and to the pumping speed of the vacuum system. The maximum pressure allowable is 1×10^{-4} torr at the mass analyzer; higher pressures result in decreased filament life. The sample under study should be of a homogeneous grain size (usually $\leqslant 100$ mesh). The thickness of the sample should not exceed 1 mm; otherwise, during gas release from the sample, a portion of the sample may be lost from the sample cup. Should this occur, the weight-loss values must be adjusted accordingly. Sample weights range from 20 mg for volatile-rich materials (such as carbonaceous chondrites, shales, or sediments containing volatile organic phases) to 500 mg for crystalline igneous rocks.

After the thermoanalyzer is programed for the desired heating rates and maximum temperatures, the background of the system is recorded on the quadrupole mass spectrometer. This background is subtracted from each subsequent spectrum made during the analysis of the sample under study. After the thermal analysis is started at the desired heating rate (usually 2°, 4°, or 6°C/min), the mass spectra are recorded at

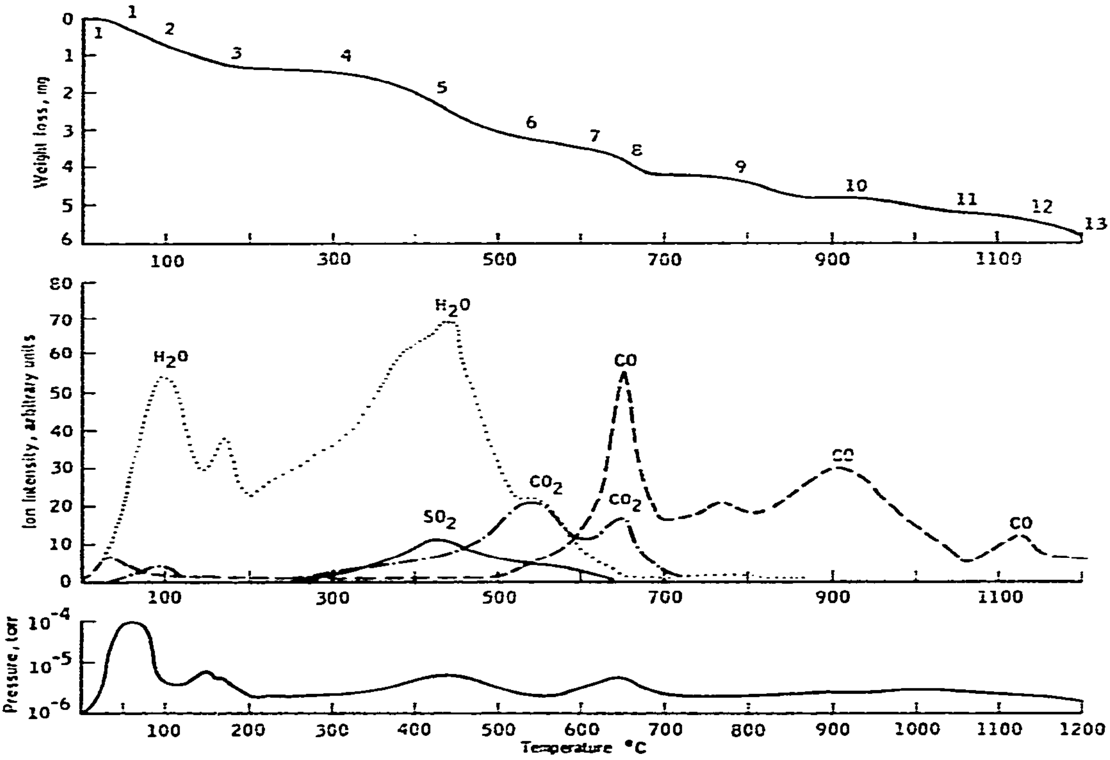

Fig. 3. Thermogravimetric-analysis–gas-evolution-analysis curves for the Orgueil carbonaceous chondrite.

regular temperature intervals, or, alternately, a single mass of interest can be monitored continuously. When the analysis is completed, a plot of the gas evolution as a function of temperature for the gaseous species of interest can be made. The correlation of the gas-release patterns with sample-weight-loss and pressure curves is made for the sample under investigation. In Fig. 3, a typical gas-evolution pattern is shown.

RESULTS AND DISCUSSION

The thermogravimetric-analysis curve, the gas-release patterns, and the pressure changes obtained from the analysis of a 21.79-mg sample of the Orgueil carbonaceous chondrite meteorite are shown in Fig. 3. The mineralogy of this meteorite has been described by Boström and Fredriksson[10] and Bass[11]. The sample was heated under an initial vacuum of 4×10^{-6} torr at a linear heating rate of 4°C/min to 1200°C. Under these conditions, the sample decomposes in several stages, releasing a multitude of primary and secondary products. Mass spectra of the released volatile components were recorded at intervals of 12.5°C. Typical spectra obtained are shown in Fig. 4.

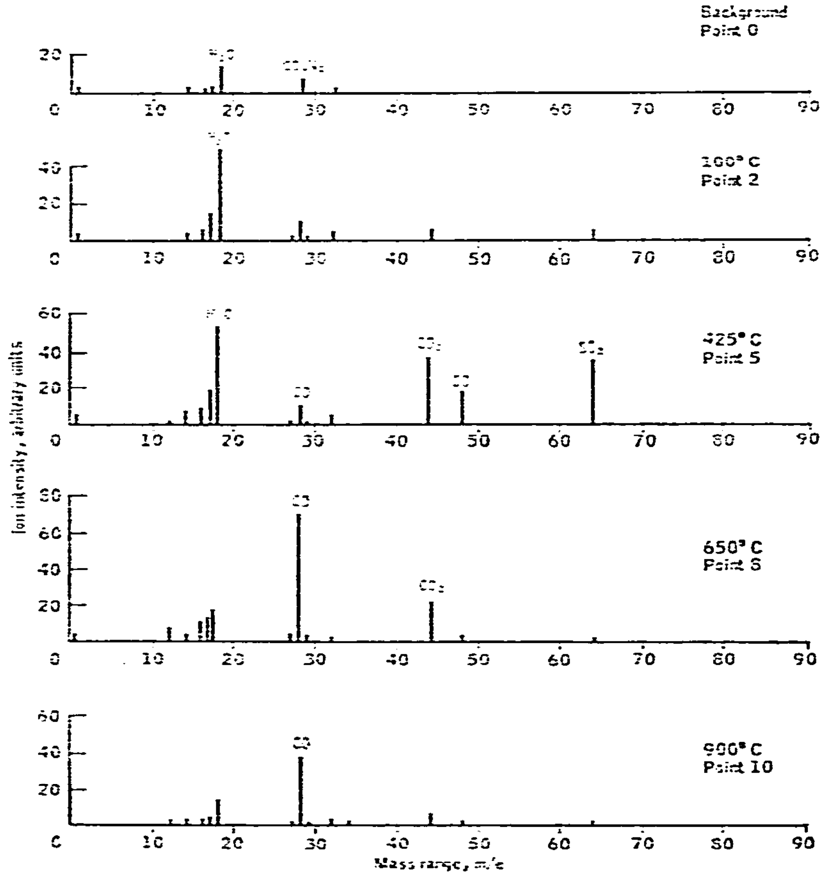

Fig. 4. Mass spectra at selected temperatures during the thermal analysis of the Orgueil carbonaceous chondrite.

The resolved analytical data obtained from the mass-spectrometric investigation are shown in Fig. 3 along with the variation in reaction-furnace pressures produced by the sample decomposition. To examine the effects of using a faster heating rate on the gas-release patterns, two additional samples of the Orgueil meteorite were analyzed at 6° and 10 °C/min. The general overall shapes of the gas-release curves were retained, but the individual gas-release patterns were shifted toward higher temperatures. The fine structure (*e.g.*, sharp gas-release peaks) of the gas-release curves is not seen at the faster heating rates.

It is apparent from the data given in Fig. 3 that the sample-weight changes, the evolved gaseous species, and the pressure changes are all directly correlated. The ion-intensity factors used in Fig. 3 were derived from the individual spectra obtained at each temperature. The background corrections were subtracted, and the resulting ion intensity was plotted. The experimentally obtained mass spectra are indicative qualitatively of the gaseous species present; the peak heights are only indicative semiquantitatively of the amounts of each volatile component present. The spectra obtained during the heating process are indicative of the sequence of appearance and disappearance of each major and minor component.

The mass spectra obtained at point 0 in Fig. 3 are the background and residual air of the system within the reaction chamber. The mass spectra in bar-graph form for points 0, 2, 5, 8, and 10 are shown in Fig. 4. These spectra were obtained at 12.5 °C intervals from room temperature to 1200 °C. It is apparent from the spectra obtained at point 2 that adsorbed water vapor, with a minor amount of carbon dioxide dissolved within the water, was released up to 125 °C. In addition, trace quantities of nitrogen were released at mass 28. Nitrogen was the sole contributor to the mass 28 peak, as was determined by examining the mass 14/mass 28 ratio along with the mass 12 and mass 16 fragment peaks. The water peak shown between 150° and 200 °C is accounted for by the dehydration of the mineral limonite, α-$Fe_2O_3 \cdot H_2O$. Apparently, at 200 °C, all of the adsorbed water had been removed from the sample.

At 300 °C (point 4), release of the interlayer, structurally bound water from the sample begins. The loss of water between 300° and 500 °C is caused by the loss of interlayer water in the montmorillonite and chlorite or similar clay minerals of the carbonaceous chondrite[11]. At point 5, sulphur dioxide from the decomposition of epsomite and gypsum is released. The chemically bound water from epsomite, $MgSO_4 \cdot 7H_2O$, and gypsum, $CaSO_4 \cdot 2H_2O$, also contributes to the larger water peak occurring between 400° and 500 °C.

At point 6, carbon dioxide is the major gaseous species present. The carbon dioxide results from the decomposition of the siderite, $FeCO_3$. The second carbon dioxide peak at point 8 is formed by the loss of CO_2 from breunnerite, $(Fe,Mg)CO_3$, and dolomite, $CaMg(CO_3)_2$. Also at point 8, the large carbon monoxide peak results from the breakdown of carbonaceous matter present in the meteorite. Higher molecular weight hydrocarbons are also evolved in this temperature region, but their identity has not been established definitely. Further work on this problem will be carried out in the future.

In the 900 °C region of the analysis, carbon monoxide is released. It is believed that this gaseous species is the product of a chemical reaction between carbon in the form of carbonaceous matter, or graphite, and the silicates present. At the temperatures within the furnace, reactions can occur to produce the observed carbon monoxide. Similar release of carbon monoxide has been produced by carrying out experiments under the same reaction conditions. Small amounts ($<5\%$ weight) of meteoritic cohenite, $(Fe, Ni, Co)_3C$, less than 200 mesh, were mixed physically with terrestrial olivines, pyroxene, and anorthite. The analysis of this mixture was indicative that the reactions at 900° and 1100 °C would produce the observed carbon monoxide.

Thermal analysis–mass-spectrometric analysis of carbonaceous chondrites is of extreme theoretical interest because the thermal-decomposition curves and gas-evolution curves cast light on the possible conditions that prevailed during, and subsequent to, the final accumulation of these volatile-rich meteorites. Further studies on other carbonaceous chondrites are presently underway in this laboratory. The technique has wide application to other areas of analysis.

ACKNOWLEDGMENTS

Assistance from F. F. Davis of Finnigan Instrument Corporation is acknowledged. H. B. Wiik provided the sample of Orgueil carbonaceous chondrite.

A portion of this work was carried out while one of the authors (E. K. G.) was a NASA-NCR Resident Research Associate in the Geochemistry Branch, NASA Manned Spacecraft Center.

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