THERMAL ANALYSIS–MASS SPECTROMETER COMPUTER SYSTEM AND ITS APPLICATION TO THE EVOLVED GAS ANALYSIS OF GREEN RIVER SHALE AND LUNAR SOIL SAMPLES

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ABSTRACT

A thermal analysis–mass spectrometer system controlled by a computer has been developed and successfully used in the analysis of a wide variety of geochemical samples. The TA–MS computer system provides a very powerful analytical tool for the determination of volatile species released from samples over a very wide temperature and sample-size range. Use of a small laboratory computer and magnetic-tape storage units permits large quantities of analytical information to be handled and easily retrieved. The rapid scan capabilities of the quadrupole mass spectrometer operating under computer control are especially useful for following the rapidly changing composition of the evolved gases released from samples during heating under vacuum conditions. Samples of volatile-rich Green River shale and two lunar soils have been analyzed to show the utility of the TA–MS computer system.

INTRODUCTION

Thermal analysis–evolved gas analysis can be applied to a wide variety of analytical problems involving thermal decompositions, phase equilibria, and the identity of released volatiles. The mass spectrometer is one of the most powerful analytical tools available to the chemist for the identification of materials that can be easily volatilized or decomposed. When the mass spectrometer is interfaced with a thermal analysis system, an even more powerful analytical tool evolves. In the laboratory, a quadrupole mass spectrometer was interfaced with a vacuum-recording thermoanalyzer. This combination has been described previously[1]. The thermal analysis–mass spectrometer (TA–MS) system generates large volumes of information on the composition of the evolved gases, their relative amounts, and temperature-release profiles. To handle these data in a convenient manner in which they can be reduced to a usable form in a short period of time, a small laboratory computer with two magnetic-tape units has been interfaced with the mass spectrometer–thermoanalyzer. The complete system consists of the following: (1) a thermoanalyzer with

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interfaced quadrupole mass spectrometer, (2) a mass spectrometer–computer interface, (3) a PDP 8/L general-purpose digital computer with a tape controller and two magnetic-tape units for data storage, (4) a digital plotter, and (5) a teletype printer. A schematic of the complete system is shown in Fig. 1. Detailed descriptions of a more complex computer-operated mass spectrometer system have been given by Reynolds et al.[2].
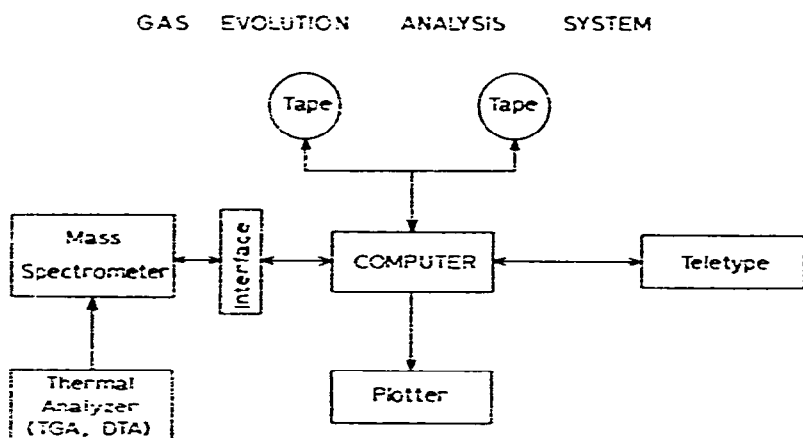
GAS   EVOLUTION   ANALYSIS   SYSTEM

Fig. 1. Schematic of gas-analysis system.

EXPERIMENTAL

Equipment

A Finnigan 1015S/L quadrupole mass spectrometer interfaced with a Mettler vacuum-recording thermoanalyzer was used in this work[1]. The computer system used with the TA–MS system was a specially modified System/150, manufactured by Systems Industries. The System/150 is normally used with a gas chromatograph–mass spectrometer system.

The Finnigan mass spectrometer is of the quadrupole type, and the ionized particles are separated according to their mass-to-charge ratio by sweeping an r.f. and d.c. voltage across the quadrupole mass-filter assembly. It consists of four molybdenum rods placed at the corners of a square. Situated at one end of the mass filter is an ionizer (rhenium filament operating at 70 eV) the function of which is to ionize the samples and direct the ions into the quadrupole assembly; at the other end of the quadrupole is an electron-multiplier detector. The ions, which have the correct mass-to-charge ratio and have passed through the quadrupole mass filter, impinge upon the first dynode of the electron multiplier. This action causes a current flow, and the analog signal is sent to the interface where it is digitized and then sent into the computer. Each voltage sweep sends a complete mass spectrum to the computer. All the data are stored on magnetic tape.

Because the scanning voltage is varied in a linear manner and because of the mass-separating qualities of the hyperbolic electric fields created within the qua-

drupole rod assembly, the final mass presentation is linear. The spacing between masses 17 and 18 is, for example, identical to that between masses 500 and 501. This condition makes computerization easy compared to magnetic analyzers. The sweep time of the quadrupole mass spectrometer can be as fast as 0.01 sec, making it an ideal instrument for scanning extremely fast eluding gas phases, such as gases released from the rupturing of vesicles and gas-rich inclusions.

The interface between the computer and mass spectrometer consists of several components. The function of the 15-bit digital-to-analog converter is to select a number typed in by the operator and convert it to an analog rod voltage. By typing in the first and last mass, the operator sets the mass range that the mass spectrometer will scan. The output analog signal from the mass spectrometer is routed to an integrator that integrates this ion current over a length of time that was initially specified by the operator. The output from the integrator is converted to digital form by a 12-bit analog-to-digital converter and is then transmitted to the computer, which normalizes and transfers the data onto magnetic tape. The timing generator is capable of generating sample times of 1 msec to 5 min. Also, it is capable of automatically adjusting the integration time as a function of signal strength. This capability provides a nearly constant signal-to-noise ratio over the entire spectrum. The interface also consists of logic and registers necessary to interface the mass spectrometer with the computer.

The computer is a small-scale, general-purpose digital system with a 12-bit word length and 4096 words of core storage. The operator communicates through the teletype with the system in a conversational dialogue (a simple yes, no, or numeric responses to computer-program-originated prompting). The software for the system has been developed by Systems Industries. The *executive* program interprets the operator's inputs from the teletype printer, loads the required programs from the magnetic tape into the computer memory, and transfers control to the particular program. *Diagnostic* routines capable of checking the performance of the interface independent of the mass spectrometer and indicating any malfunctions that may occur are also available. In addition, there are *utility* and *maintenance* programs consisting of LIST, COPY, WRITE, DUPLICATE, and DELETE routines.

Normal calibration of the mass spectrometer–computer system requires approximately 40 sec. The calibration reference samples consist of an air–rare-gas mixture (air, helium, argon, and krypton) for the mass range 1–100 and an organic compound FC-43 (perfluorotributylamine) for higher mass ranges (50–750). The calibration samples are introduced into the mass spectrometer, the system automatically calibrates on the reference samples, and a tape file with the calibration data (mass number relative to mass set voltage) is originated.

Operational modes

Two separate modes of operation possible with the System/150 are (1) *data logging* and (2) *spectrum control.* These two approaches differ only in the way that they acquire data; the analytical process is the same for both.

Using the *data logging* approach to data acquisition, the control operations of the mass spectrometer and thermoanalyzer are designated by the operator. The mass spectrometer operates semi-independently of the computer, scanning the spectrum and measuring ion intensity at all mass points within the range of scan. The computer reduces these raw data and presents the analytical results in a mass spectrum in the form of relative abundance versus mass units (or time) on a scale of 0–100.

Spectrum control is an approach to data acquisition made possible by the development of the quadrupole mass spectrometer. Using spectrum control, the computer controls the operation of the mass spectrometer as well as analysis of the results. The operator specifies the analytical data to be obtained, and the computer does the necessary tasks. During the analysis of samples, the operator decides the operating conditions for the thermal analysis (*e.g.*, heating rate, sample size, weight sensitivity, maximum desired temperature). By matching the operating parameters of the thermoanalyzer and mass spectrometer, the samples are heated at programed rates (linear or isothermal) and the mass spectrometer, under computer control, measures the ion intensities at those mass points that have been designated. Other mass points are not sampled. By computer commands to the mass spectrometer, the gases coming from the sample are analyzed at set periods of time (*e.g.*, any time interval between 1 sec and 5 min). The composition of the gases evolved from the sample can be determined as a function of temperature by correlating spectrum number with the recorded sample temperature. For example, if the heating rate were 6°C/min and the mass spectrometer sampled the gases every 10 sec, a mass spectrum of the gaseous composition would be collected at every 1°C interval during the heating period.

The selective scanning technique (sampling only designated masses or mass ranges) can increase the effective scan speed of the mass spectrometer for a given sampling rate. This capability is particularly helpful in operating the mass spectrometer in a repetitive scan mode, such as when it is interfaced with the thermoanalyzer or a gas chromatograph. The total amount of data that has to be recorded is reduced, and, by permitting more scans for a given time period, the resolution of the ion-intensity-versus-time information is also improved.

When spectrum control or computer-controlled data acquisition is used, the following parameters for each analysis can be set by the operator:

(1) Scanning continuous and noncontinuous mass ranges (up to eight separate mass ranges) and acquiring only relevant data, thus increasing the effective scan speed.

(2) Specifying different integration times for different mass ranges, thus enhancing the sensitivity of the instrument.

(3) Specifying sampling rates per a.m.u. to detect mass defects and to determine isotopic ratios accurately.

(4) Specifying threshold levels to suppress background noise of the entire system.

(5) Using the automatic adjustment of integration times as a function of signal

strength in the signal optimization mode, resulting in a nearly constant signal-to-noise ratio.

(6) Determining conditions for the thermal analysis–mass spectrometric analysis, specifying the maximum run time and allowing the instrument to remain unattended with the assurance that all desired data will be acquired and that no evolved gases will be missed in the mass ranges specified.

Output routines

The *data output mode* is used to output information stored on the magnetic tape from the TA–MS computer analysis of samples. During the mass spectrometer control and data-acquisition phase, the plotter gives a real-time gas-release pattern. At the end of the analysis, the computer can also plot a reconstructed gas-release pattern which normalizes on the largest peak or gas-release region. The real-time gas-release pattern is simply a plot of the ion current from the electron multiplier at each recorded spectrum scanned. In addition to the real-time gas-release pattern, the following output routines are available:

(1) Reconstruction of a gas-release pattern that normalizes the largest gas-release peak or region to 100 and indexes the mass spectra acquired during the run.

(2) Printed or plotted spectra from any mass spectrum collected.

(3) Plots of individual mass (*e.g.*, mass 18) peaks as a function of temperature, providing information on the temperature region of greatest gas release.

(4) Spectrum plots or printouts with positively identified mass scales and numeric ion intensities.

(5) Spectrum plots or printouts with the background spectra subtracted to eliminate the effect of contaminants or backgrounds.

The TA–MS computer system has been used to identify volatiles released during the heating, their abundances, temperature-release ranges, and sequence of release. By combining the evolved gas information with the thermal analysis data, complete characterization of the decomposition path for a wide variety of materials can be obtained. The analytical technique has been successfully applied to the analysis of lunar samples, meteorites, minerals, terrestrial rocks, and volcanic ashes in addition to volatile-rich materials such as oil-rich shales, paints, plastics, and polymers. A detailed discussion of the analysis of the volatile-rich Green River shale and the volatile-depleted Apollo 14 and 15 soils will be given to show two applications of the TA–MS computer system.

Green River shale pyrolysis

The Green River shale is an oil-rich material that contains up to 35% volatiles[3]. Detailed discussions of the volatiles and organic compounds found in this oil-rich shale have been given by Forsman[4] and by Robinson[5]. Recently, Smith and Johnson[6] have discussed simultaneous DTA–TG–MSA studies of Green River shale components and similar oil-rich shales. This discussion of Green River shale analysis will be restricted to the application of the TA–MS computer system to the

analysis of a 6.0-mg sample of the oil-rich shale. The sample analyzed had been ground to pass through a 100-mesh sieve ($-147\ \mu$). The sample holder used was an 8-mm-diameter, flat, platinum, dish-type holder resting directly on the Pt/Pt–10% Rh thermocouple. The sample had been evacuated to 10^{-6} torr; a 10°C/min heating rate was used. During analysis, the sample weight, temperature, and composition of the evolved gases were recorded. The reconstructed thermal-analysis curve and gas-release profile for the sample analyzed are shown in Fig. 2.
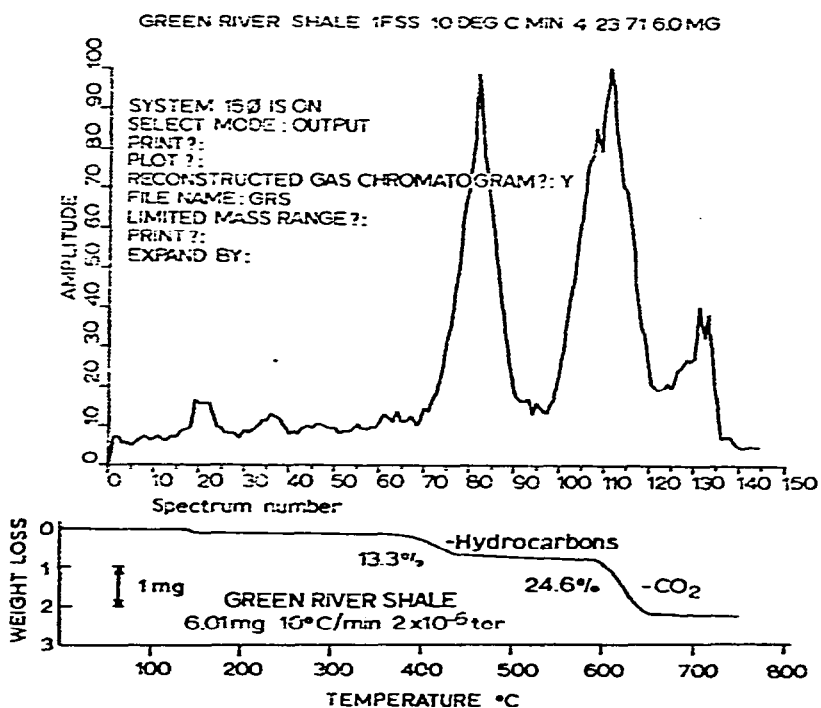

Fig. 2. Weight-loss curve and gas-release profile from analysis of a 6.0-mg sample of Green River shale.

Green River shale lost weight in two distinct regions. The two large weight losses were exactly matched by the two gas-release peaks. Excellent agreement existed between the weight-loss regions and the evolved-gas peaks (Fig. 2). When heated to approximately 375°C, the sample began to lose weight and continued to do so until the temperature reached 450°C. The weight loss in this temperature interval was 13.3 weight percent. The gas-release patterns shown in Fig. 2 exhibit a peak for the gases between spectrum numbers 71 and 90. The compositions of these evolved gases (spectrum number 77) are shown in Fig. 3. Mass spectrum number 77 shows the typical hydrocarbons of masses 27, 29, 39, 41, 55, 57, and 69. In addition, small traces of H_2O (mass 18) and CO and/or N_2 (mass 28) are also present. To determine the temperature range in which the hydrocarbons are released, the release profile for mass 55 (which is a typical hydrocarbon fragment) has been plotted in Fig. 4. The
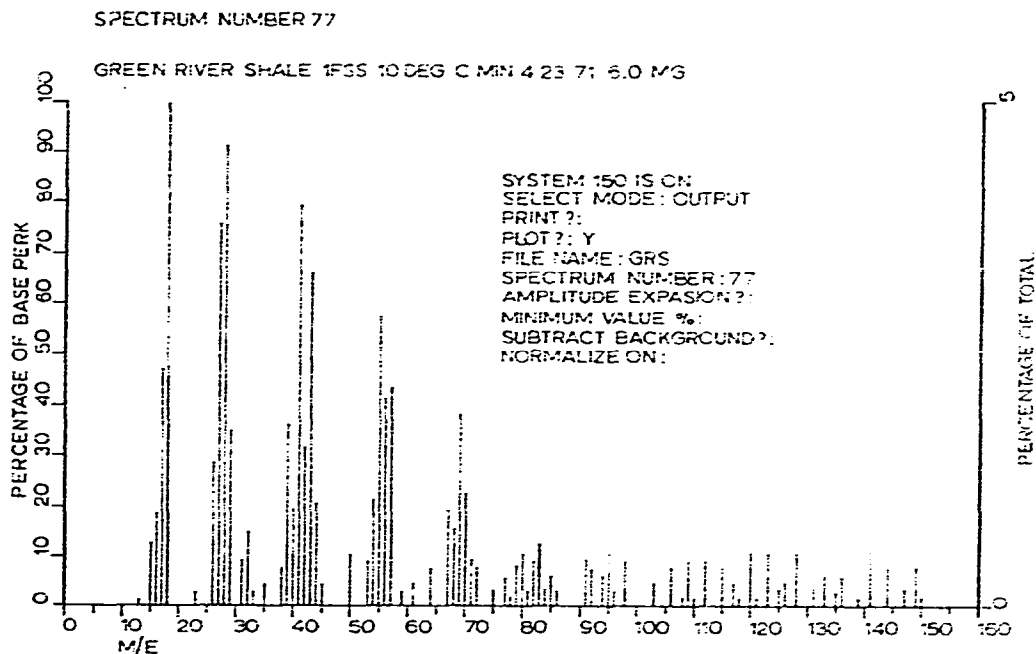
SPECTRUM NUMBER 77

GREEN RIVER SHALE 1FSS 10 DEG C MIN 4 23 71 6.0 MG

SYSTEM 150 IS ON
SELECT MODE : OUTPUT
PRINT ?:
PLOT ?: Y
FILE NAME : GRS
SPECTRUM NUMBER : 77
AMPLITUDE EXPASION ?:
MINIMUM VALUE %:
SUBTRACT BACKGROUND ?:
NORMALIZE ON :

Fig. 3. Mass spectrum of gases released at 400°C. Spectrum shows the presence of numerous hydrocarbon fragments along with trace quantities of H_2O and CO.

GREEN RIVER SHALE 1FSS 10 DEG C MIN 4 23 71 6.0 MG

SYSTEM 150 IS ON
SELECT MODE :OUTPUT
PRINT?:
PLOT?:
RECONSTRUCTED GAS CHROMATOGRAM?: Y
FILE NAME : GRS
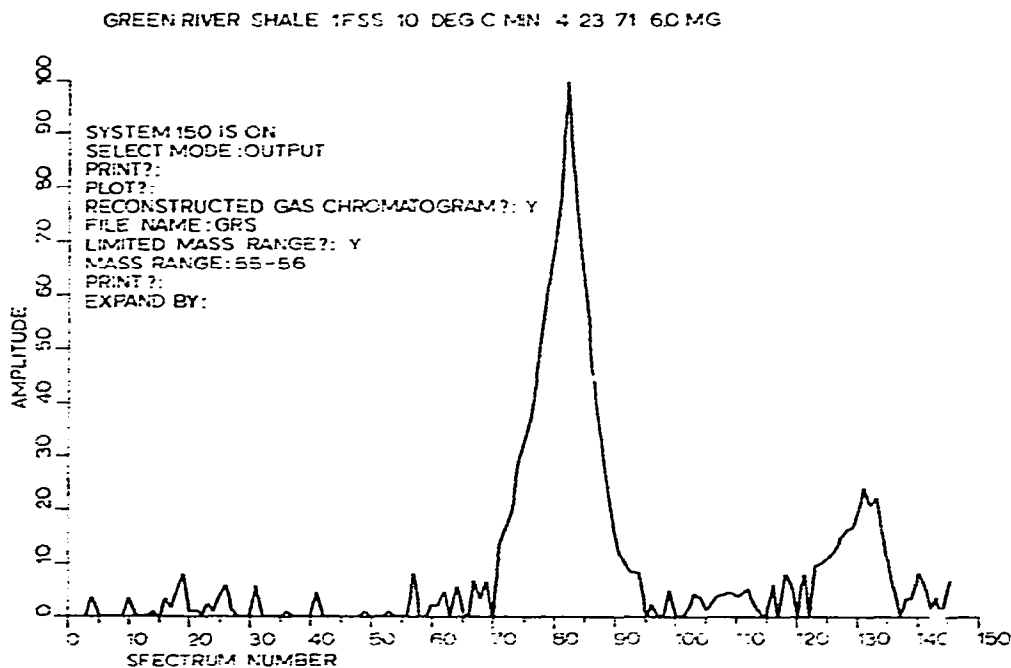LIMITED MASS RANGE?: Y
MASS RANGE: 55-56
PRINT ?:
EXPAND BY:

Fig. 4. Reconstructed gas-release profile of mass 55. The major peak results from hydrocarbon fragments released in the 390–450°C temperature range. The minor peak at spectrum numbers 120–135 results from the pyrolysis of trace quantities of condensed hydrocarbons in the analysis system.

250

GREEN RIVER SHALE 1FSS 10 DEG C MIN 4 23 71 6.0 MG

SYSTEM 150 IS ON.
SELECT MODE:OUTPUT
PRINT?:
PLOT?: Y
FILE NAME:GRS
SPECTRUM NUMBER:103
AMPLITUDE EXPANSION?:
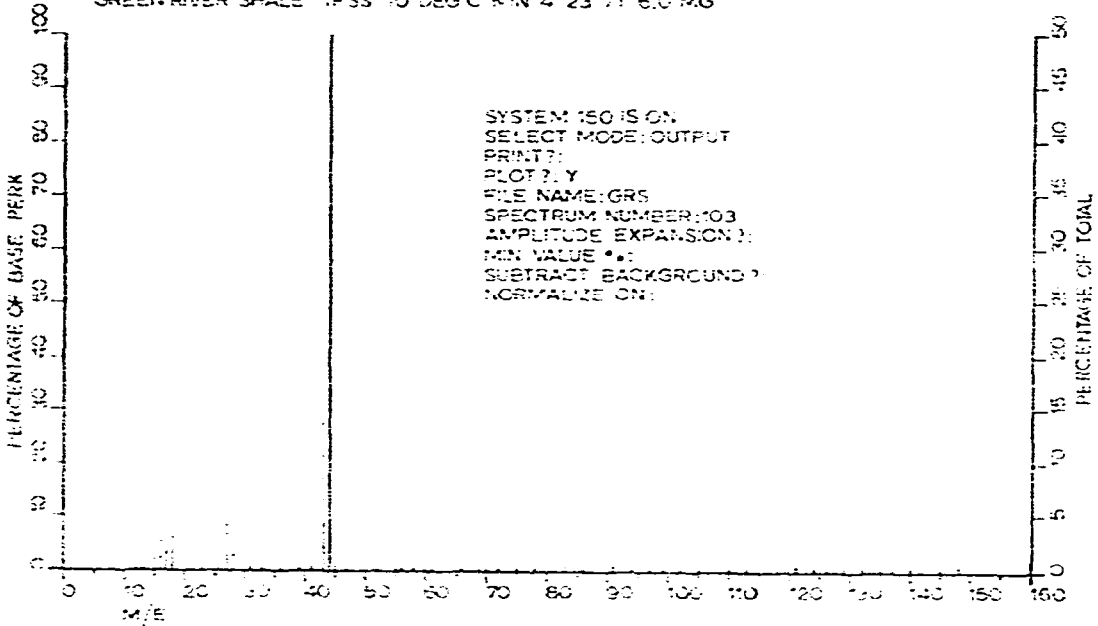MIN VALUE *:
SUBTRACT BACKGROUND?
NORMALIZE ON:

Fig. 5. Mass spectrum of gases released at 600 °C. Spectrum shows the presence of only CO_2 resulting from decomposition of carbonate phases.

GREEN RIVER SHALE 1FSS 10 DEG C MIN 4 23 71 6.0 MG

SYSTEM 150 IS ON
SELECT MODE:OUTPUT
PRINT?:
PLOT?:
RECONSTRUCTED GAS CHROMATOGRAM?: Y
FILE NAME:GRS
LIMITED MASS RANGE: Y
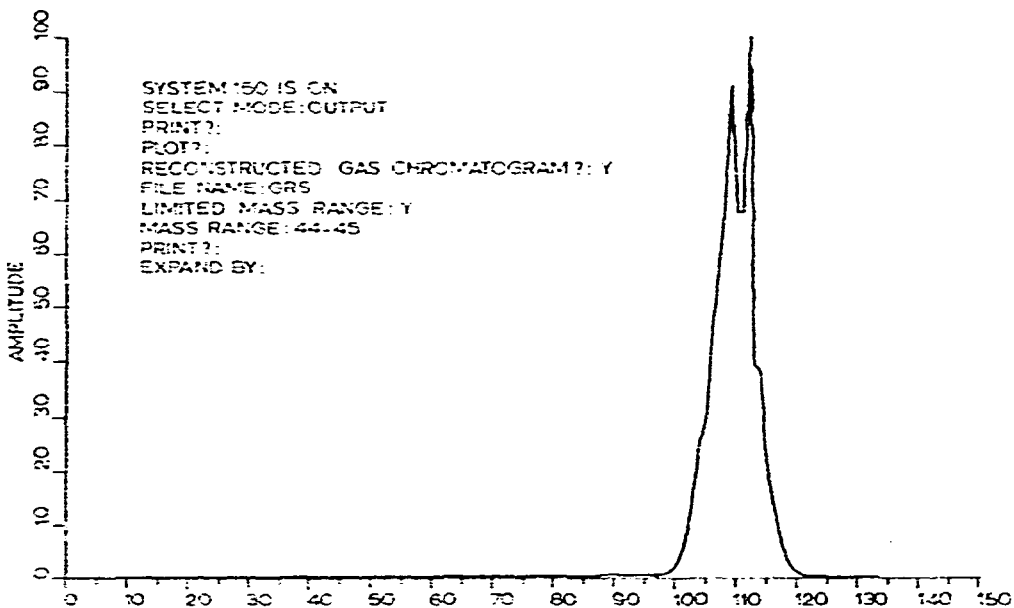MASS RANGE: 44-45
PRINT?:
EXPAND BY:

Fig. 6. Reconstructed gas-release profile of mass 44. The gas-release profile shows that CO_2 is released only between spectrum numbers 100 and 120.

release of the mass 55 is restricted to spectra 71 to 90 with perhaps minor amounts (less than 15% amplitude) released at temperatures above 700°C.

The Green River shale sample loses 24.6 weight percent between 590 and 650°C. This weight loss results from the decomposition of carbonate phases found in the oil-rich shale. The carbonate phases have been discussed by Smith and Johnson[6] and consist of nahcolite, dolomite, dawsonite, and "ferroan". The mass spectra of the evolved gases between temperatures 590 and 650°C (spectra 100 to 120) are shown in Fig. 5. Mass 44 (CO_2) was the only peak that appeared in the spectra. A reconstructed gas-release profile for mass 44 is shown in Fig. 6. The spectrum number given in Fig. 6 is directly correlated with the temperature given in Fig. 2. The single peak for mass 44 between spectrum numbers 100 and 120 indicates that CO_2 is released only between 590 and 650°C. It is interesting to note that the two small spikes on the top of the CO_2-release profile (Fig. 6) are very similar to those observed previously for the decomposition of dolomites found in meteorites[1].

Lunar soil pyrolysis

Lunar samples present a unique requirement that the analyst obtain the maximum amount of useful information on a minimum sample size. The lunar samples from the six previous lunar missions (Apollo 11, 12, 14, 15, and Luna 16 and 20) are all depleted in their volatile elements (*e.g.*, C, N_2, S, Na, and K) and compounds such as hydrates, carbonates and sulfates[7-10]. The lunar soils are complex
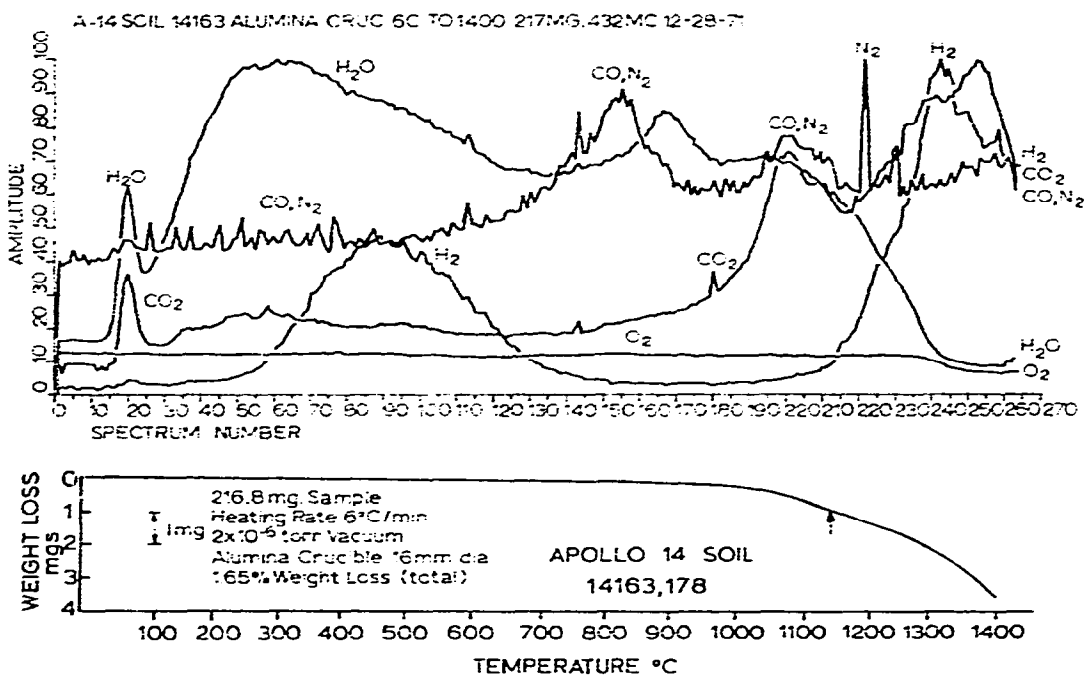

Fig. 7. Weight-loss curve and gas-release profile for Apollo 14 soil 14163,178. The presence of H_2O and CO_2 being released from the sample at temperatures below 150°C should be noted. The arrow on the weight-loss curve around 1140°C indicates the initial melting of the sample.
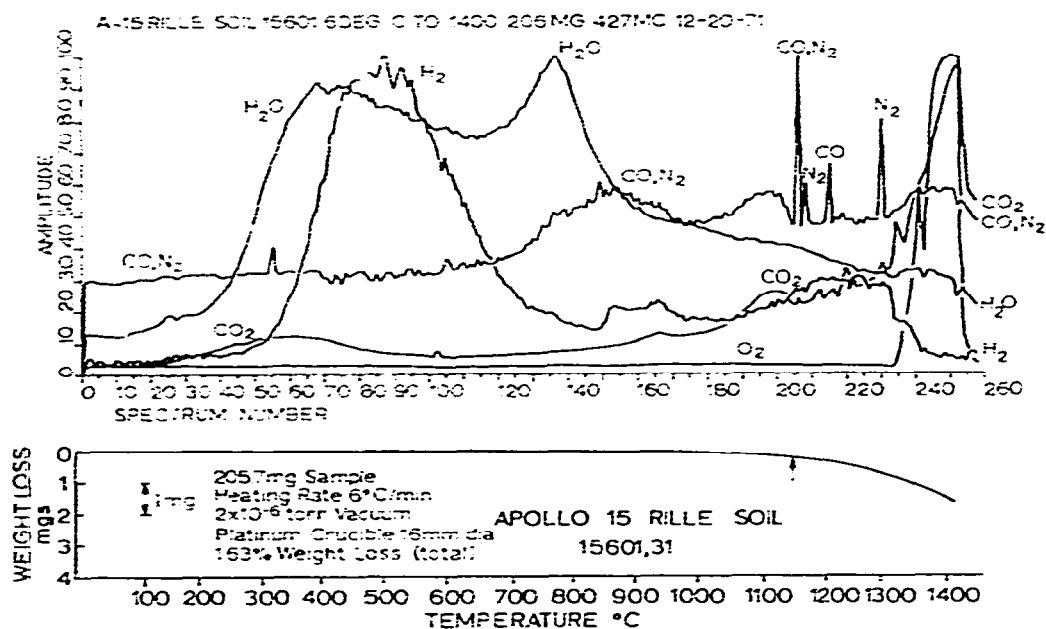
Fig. 8. Weight-loss curve and gas-release profile for Apollo 15 soil 15601,31 from Hadley Rille. The spikes on the gas-release curves for CO and N_2 should be noted. These spikes undoubtedly result from rupturing of vesicles and gas-rich inclusions. The release of O_2 at 1300 °C results from the dissolution of Fe into the platinum crucible, releasing O_2. The absence of the sudden release of O_2 when the samples are heated in an alumina crucible (Fig. 7) should be noted.

mixtures of individual mineral grains, glass particles, rock chips, and trace quantities of meteoritic components. Thermal analysis–inorganic gas-release studies have been performed on samples from each of the four Apollo lunar missions[11,12]; DTA has shown[12] that the lunar soils undergo melting in the region of 1080–1250°C.

Because of the depletions in the volatile components in lunar samples, the small weight-loss measurements (TG) on lunar samples are not surprising. A TG and gas-release profile for the Apollo 14 soil collected near the lunar module and for the Apollo 15 soil from Hadley Rille are given in Figs. 7 and 8, respectively. Lunar soils analyzed from the first four Apollo missions lose less than 0.35 ± 0.10 weight percent when heated to 1000°C under vacuum of 10^{-6} torr, and even after 1400°C the soils lose less than 1.70 ± 0.50 weight percent. These weight-loss studies were performed on soil samples ranging in weight from 200 to 225 mg. The soil samples were analyzed in 16-mm-diameter platinum and alumina crucibles. The small weight losses measured are indicative of the past thermal histories of these complex samples.

A separate sample of Apollo 14 soil 14163,178 heated to 1400°C in air gained 4.80 weight percent. The weight gain resulted from the oxidation of iron and other reduced phases in the soil samples. The lunar samples had been formed under extremely low partial pressures of oxygen, and the absence of iron in the ferric state is to be expected[7–10]. The weight gain from heating lunar soil samples in air perhaps could be used as an indicator of the relative degrees of reduction for the various soil

samples. Hanneman[13] previously reported a net weight gain when the lunar soils were heated under oxidizing conditions.

The small weight losses that result during heating of lunar soils in vacuum do not encourage one in his attempt to locate and determine the volatile phases released from the lunar soils; however, the high sensitivity of the mass spectrometer shows that numerous volatile gas species are released during the heating of the samples (Figs. 7 and 8). The gas-release patterns obtained from the lunar soils indicate that gaseous species originate from several sources. Evidence has been obtained indicating that the gases are: (1) contaminants, (2) solar-wind-derived species, (3) reaction products, and (4) gas phases within vesicles and gas-rich inclusions[11,12].

Thermal analysis–inorganic gas-release studies of the lunar soils have shown that very little volatile-rich materials or hydrous mineral phases are found in the lunar soils[11,12]. The gases released during the heating of the soils result from separate and distinct sources. Water vapor and CO_2 have been adsorbed by the lunar soils that have been exposed to the terrestrial atmosphere after return to earth. These two gaseous species are loosely bound to the surfaces of the soils and are lost from the samples when they are heated under vacuum at temperatures below $150°C$. The Apollo 14 soil sample (Fig. 7) had been exposed to the atmosphere for 1 month before analysis, while the Apollo 15 soil (Fig. 8) had been stored under N_2 since return from the moon and was not exposed to the atomsphere until the analysis began. The effects of exposure of the lunar soils to the atmosphere can be seen by the differences in the gaseous species released at temperatures below $150°C$ (Figs. 7 and 8).

Solar-wind components such as H_2 and He and possibly CO_2 are trapped within the outer surfaces of individual mineral and glass grains, and these gases are released between 300 and $700°C$. Additional low-molecular-weight species such as H_2O (possibly in the hydroxyl form) can be formed on the outer surfaces of rocks and mineral grains as the result of proton irradiation from the solar wind. Initial laboratory experimental results from irradiation with 100-keV protons on lunar analogs produce trace quantities of H_2O, and the temperature-release profile along with the concentration of H_2O produced is similar to that released from lunar samples[12].

The release of the gaseous species CO, CO_2, H_2S, and SO_2 at temperatures above 600°C result from the reaction products of C- and S-containing phases found with mineral and glass found in the soils. The S-containing gaseous phases (SO_2 and H_2S) are released between 1000 and 1300°C and are derived from reaction of troilite and other sulfides with the silicate phases at elevated temperatures. Identical gas-release profiles have been produced using lunar analogs[11]. The S-containing gases have not been plotted in Figs. 7 and 8 to prevent cluttering the figures.

The presence of gas phases in vesicles and gas-rich inclusions along with those gases exsolving from the melt is shown by the gas spikes around 1140°C in Figs. 7 and 8. The gases present are CO or N_2 or a combination of the two. These gas phases are released as sudden bursts of gas at temperatures immediately above the melting point ($1130 \pm 20°C$) of the samples. The identity of the gases found are similar to those that

should be expected from theoretical considerations of the lunar gaseous environment during the time of crystallization of the lunar samples[14].

CONCLUSIONS

The analytical technique of combined thermal analysis-mass spectrometric computer control has been successfully developed and applied to the analysis of a wide variety of geochemical samples. Samples analyzed have ranged from oil-rich shales, which contain large quantities of volatile components, to lunar soil samples, which have been depleted in their volatile content. The TA–MS computer system provides a very powerful tool for the analysis of volatile components released from samples over a very wide temperature and sample-size range. The use of the small laboratory computer and magnetic-tape units for the storage of the analytical data allows large quantities of information to be reduced easily. The capability of the data-output system to provide a gas-release profile of a single mass as a function of temperature is very convenient. The rapid scan capabilities of the quadrupole mass spectrometer are especially useful to follow the rapidly changing composition of the evolved gases. This technique can be used in other fields of analysis where, upon pyrolysis of samples, the composition of the released gas phases as a function of temperature is desired.

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