

AN EVOLVED GAS ANALYSIS SYSTEM*

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ABSTRACT

A system is described which is capable of mass spectrometrically analyzing the gaseous species evolved from a substance when heated either isothermally or at a programmed rate in the range of 100-1300°C. The system is automated to provide punched paper tape output suitable for computer analysis of the data. A calibration procedure is described using the decompositions of CaCO_3 and $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ as examples. As an example of the value of the technique, a preliminary look at zinc and oxygen loss from several ferrites is presented.

INTRODUCTION

Evolved gas analysis (EGA) with a mass spectrometer has proved to be a widely useful technique. Some inorganic applications have been traditional high temperature equilibria involving Knudsen cells, e.g. vaporization of ZnO^1 ; evaluation of products in complex decompositions^{2, 3} and determination of chemisorbed gases in thin films⁴, bulk material⁵ or catalysts⁶. The technique has been used by itself or coupled with other methods such as thermogravimetry⁷. Polymers have been studied by more sophisticated techniques such as laser degradation and modulated molecular beams in order to better subtract the background and distinguish between parent and fragment species relationships⁸. Substantial use of EGA has also been made to study materials for space applications⁹.

It is the purpose of this paper to describe an apparatus which is highly sensitive for both condensable and noncondensable gases over a wide temperature range. Particularly noteworthy is that (1) linear heating rates, from 0 to 400°C min⁻¹, are conveniently attained with a relatively well defined sample temperature; (2) the diffusion paths are very short so that time lag, condensation, and reactions with the environment are minimal; and (3) data collection and presentation can be accomplished in a variety of modes depending upon the desired application. Methods are described for obtaining quantitative information. Finally, the usefulness of such an apparatus is illustrated with a preliminary look at Zn loss from selected ferrites.

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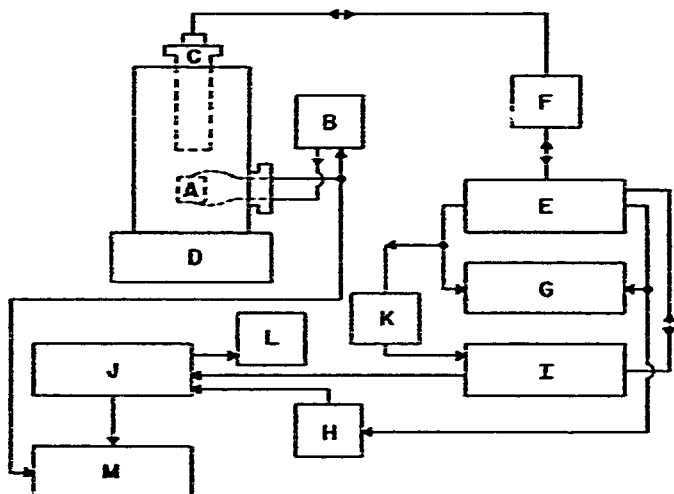


Fig. 1. Block diagram of EGA apparatus. A, Furnace, RADAC-X; Luxel Co.; B, furnace controller, Speedomax; SCR, stepdown transformer, Leeds and Northrup Co.; C, quadrupole mass spectrometer head 100C, UTI Co.; D, turbomolecular pump 2404 D, Sargent Welsch Co.; E, control unit mass spectrometer 100C, UTI Co.; F, RF unit mass spectrometer 100C, UTI Co.; G, scope 130C, Hewlett Packard Co.; H, relay; I, MS programmer QPG101, Balzar Co.; J, integrator CRS-204, Columbia Scientific Co.; K, voltage divider, 1/10; L, teletype 33, Teletype Co.; M, recorder 3000-2pen, Houston Instrument Co.

EXPERIMENTAL PROCEDURES

Figure 1 is a block diagram of the EGA apparatus. The sample is heated in a small Mo furnace, A, containing an Al_2O_3 crucible of 1 cm^3 capacity. A machined insert of Al_2O_3 is generally used which provides a thermocouple well and allows for much smaller crucibles of Al_2O_3 or Pt.

The choice of crucible is based upon any potential reaction with the sample and the volume of sample required. The latter is chosen so as not to evolve enough gas to raise the pressure in the system above about 5×10^{-6} Torr during decomposition or outgassing. Since the pumping speed is essentially constant, the fraction of weight loss and temperature profile are the primary factors which influence the selection of sample size.

The furnace is inserted into a vacuum chamber through a convenient quick-connect port that includes the electrical feedthrough for the thermocouple (Pt-Pt 10% Rh) and for the low voltage-high current required by the furnace and supplied by the programmer controller, B. The chamber also includes two view ports at the furnace level spaced 180° from each other, an ion gauge directly opposite the furnace port, and a variable leak for calibration purposes or sampling from atmospheric pressure. Using the leak, EGA can be accomplished for noncondensables in carrier gas streams at higher pressure.

The upper flange supports the head of the quadrupole mass spectrometer, C, positioned about 1 in. directly above the furnace. Included on this flange are a thermocouple gauge, a toggle valve to the atmosphere, and a bellows valve used for back-

filling the system with He. The chamber is evacuated by a turbomolecular pump, D, to a pressure of $\leq 1 \times 10^{-8}$ Torr in the absence of outgassing by the sample.

The control unit of the mass spectrometer, E, gives an output of 0–10 V which is proportional to the range of atomic mass number selected from 0 to 300 a.m.u.

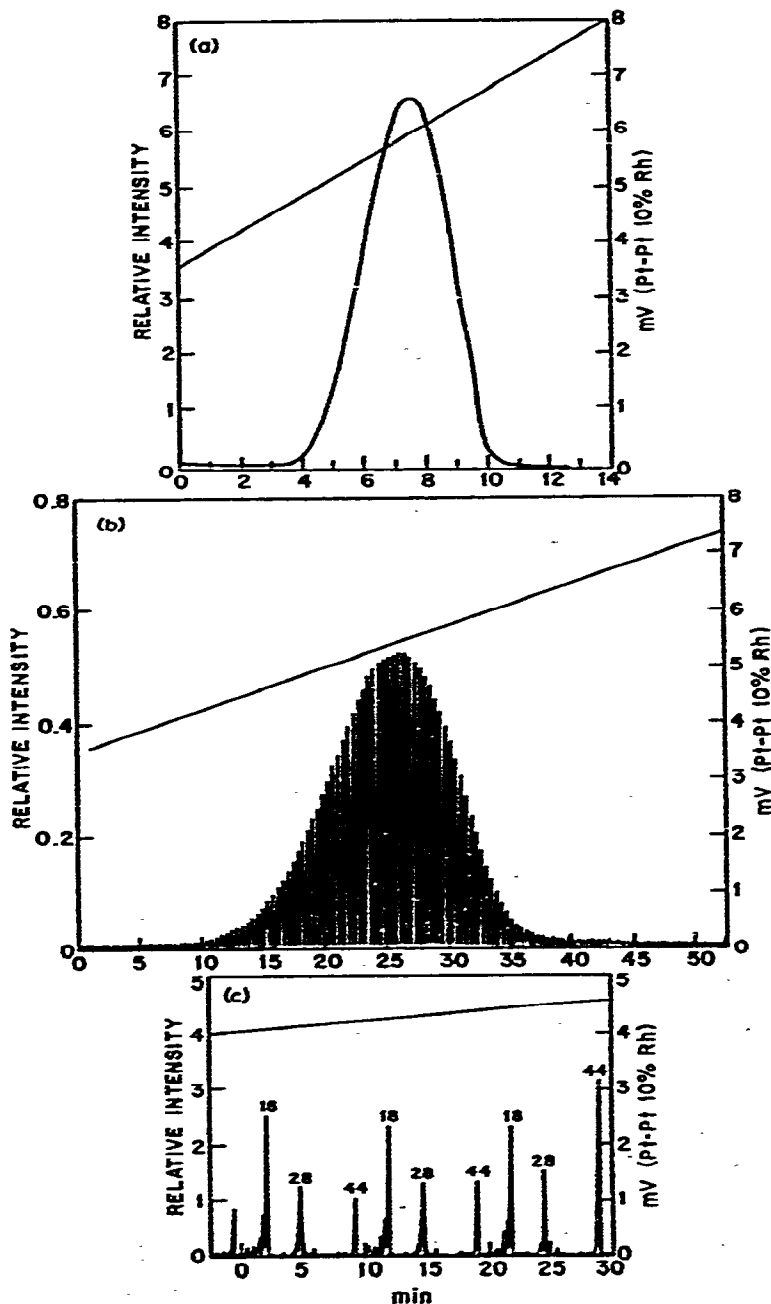


Fig. 2. Types of EGA curves and heating curve. (a) No scan, mass 44, 0.81 mg CaCO₃, 1600°C/h. (b) Short scan, mass 44, 0.79 mg CaCO₃, 400°C/h. (c) Long scan, 0–45 a.m.u., 0.54 mg CaCO₃, 100°C/h.

This signal is used for the oscilloscope, G, display and its return to 0 V is used to trigger a relay H which signifies the beginning of a new scan in the data collection system. The actual scanning rate and range can be controlled over a wide range by the spectrometer controls or by the auxiliary programmer I. The latter can select 1–12 ranges of a.m.u. to be scanned with essentially no lost time between ranges and with the option of a factor of ten additional amplifications for the individual ranges.

The output of the mass spectrometer which is proportional to the intensity of the mass peak is fed directly to the oscilloscope. This presentation is used for a simple check of the mass spectrum or for initially setting the mass range and degree of amplification. The signal directly from the spectrometer is 0–10 V and requires attenuation prior to entering the integrator J. This is accomplished by a simple voltage divider network of resistors, K. The integrator will determine the area of each mass peak and the time at the peak. The time scale is reset with each scan by means of the signal from the relay H. As a consequence, the time is an accurate indication of the particular a.m.u. and is used to establish this in subsequent data processing. Both the time of the peak and the area are listed and punched on paper tape by the Teletype L. The mass spectrum and temperature are monitored as a function of time on a two-pen recorder, M.

A variety of modes of operation are possible. The gases evolved can be studied as a function of sample temperature or isothermally as a function of time. The small thermal mass of the furnace and the insulation provided by the vacuum allow for heating rates as high as $400^{\circ}\text{C min}^{-1}$. Three methods of data presentation are generally used. Figure 2 illustrates these techniques with the recorder output for the thermal decomposition of CaCO_3 . If only one mass peak is of interest, then the spectrometer can be adjusted to that peak position and not scanned. An example is shown in Fig. 2(a). Here a smooth trace is obtained based upon the concentration of CO_2 ; however, the signal is very dependent upon instrumental drift because of the large change in intensity with a slight change in apparent a.m.u. associated with a steep peak.

This dependency upon drift can be eliminated by scanning over a short range of a.m.u. which is sure to include the peak. A smooth envelope can then be drawn through the peaks as shown in Fig. 2(b). This approach can also be used for several peaks by use of the scan programmer. Each scan can be made to include up to 12 brief segments or mass peaks. The total time of the scan would be based upon the time resolution possible on the recorder and separate envelopes could be traced for each mass.

The third alternative utilizes a much greater scan so that information can be obtained on changes over a wide range of masses. The time of a complete scan usually varies from 1 to 10 min and therefore fewer points are obtained for each mass but an overall picture of the decomposition or process is obtained. A number of scans during the decomposition of CaCO_3 are shown in Fig. 2(c). If the rate of scanning allows, about 2 sec/a.m.u., then the integrator can be used to provide the data on punched paper tape for subsequent computer analysis and plotting.

A Fortran program was written to transfer all the data from the punched paper

tape onto a storage file and to then scan the relevant data for up to 20 mass peaks. The intensities associated with these peaks are normalized by setting the maximum observed intensity from the selected peaks equal to 100. The data are tabulated by mass number listing the scan number, the intensity, the total elapsed time and, where applicable, the temperature based upon a linear heating rate. Plots of each set of data are made as a function of either time or temperature.

RESULTS AND DISCUSSION

Semiquantitative calibration In work in progress on the extent of bonding or occlusion of CO_2 and CO in various metal oxide films, at least semiquantitative data as well as qualitative data is desired¹⁰. If the pumping speed is relatively constant, then such estimates can be obtained by comparison of the areas under the curves, such as in Fig. 2(a) and (b) or the computer curve generated from data like that in Fig. 2(c), with similar curves obtained using compounds which evolve a known amount of CO or CO_2 . Naturally, the cracking patterns of the gases and the extent of the disproportionation of CO [eqn. (1)] must be taken into account.



The latter will, unfortunately, be highly variable depending upon the temperature and catalytic properties of the environment.

Figures 3 and 4 show computer-generated plots for masses 28 and 44 during the thermal decomposition of known amounts of CaCO_3 and CaC_2O_4 , respectively. The

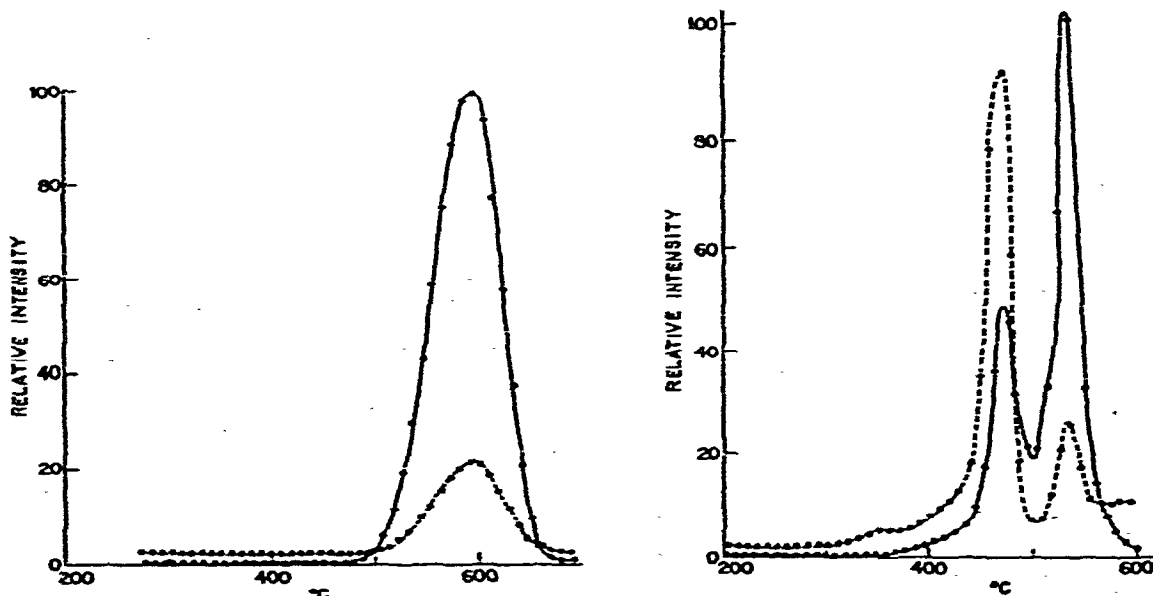


Fig. 3. EGA plots for 1.21 mg CaCO_3 at $100^\circ\text{C}/\text{h}$. —, Mass 44; ----, mass 28.

Fig. 4. EGA plots for 1.4 mg $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $50^\circ\text{C}/\text{h}$. —, Mass 44; ---- mass 28.

simpler nature of the decomposition of CaCO_3 , makes it the appropriate place to begin the analysis. Based upon linear heating and scanning rates and the assumption of a constant pumping speed independent of the pressure over the range of use, it is possible to determine a proportionality constant to relate the area under the curve in Fig. 3 with the grams of CO_2 evolved.

$$g_{\text{CO}_2} = \frac{F_{\text{CO}_2} A (\text{a.m.u./sec})(\text{area})(I_{\text{max}}/100)}{(^{\circ}\text{C}/\text{sec})} \quad (2)$$

where F_{CO_2} is the proportionality factor, A is the amplification setting from the mass spectrometer, (a.m.u./sec) is the scanning rate, (area) is the area under the curve in units of relative % \times $^{\circ}\text{C}$, ($I_{\text{max}}/100$) is the denormalization factor to correct from relative intensity to counts associated with the appropriate peak and ($^{\circ}\text{C}/\text{sec}$) is the heating rate. Substitution of the appropriate parameters associated with Fig. 3 gives

$$(0.00121)(0.44) = \frac{F_{\text{CO}_2} (10^{-7})(0.0606)(7.87 \times 10^3)(86478.16)}{0.01609} \quad (3)$$

and therefore

$$F_{\text{CO}_2} = 2.08 \times 10^{-6} g_{\text{CO}_2}/\text{count} \quad (4)$$

for this particular integrator. Similar experiments done six months later after cleaning and retuning the mass spectrometer gave a value of $2.32 \times 10^{-6} g_{\text{CO}_2}/\text{count}$ using 0.54 mg of CaCO_3 and twice the previous heating rate. The normalized cracking pattern for CO_2 associated with these experimental conditions is 44 = 100, 28 = 19.3, 16 = 18.7, 12 = 10.5, 45 = 1.07, and 22 = 0.63.

With this information for CO_2 , it is possible to attack the more complicated case of CaC_2O_4 (Fig. 4) and to extract a less accurate factor for CO. The overall decomposition scheme is



However, upon the evolution of CO, eqn. (1) comes into play and some C and CO_2 are also formed. During the subsequent decomposition [eqn. (6)], the C which was formed earlier now reacts according to the reverse equilibrium of eqn. (1) and converts some of the CO_2 to CO. Using the factor determined for CO_2 , the application of eqn. (2) to the first CO_2 peak in Fig. 4 indicates that 3.169×10^{-6} values of CO_2 were evolved during the reaction at 470°C . It is assumed that an equal amount of C is formed according to eqn. (1). Hence the actual amount of CO present is the theoretical amount 8.262×10^{-6} moles - $2 \times (3.169 \times 10^{-6}$ moles) or 1.924×10^{-6} moles of CO. Therefore the area under the CO peak at 470° should be associated with this substantially reduced amount of CO. A further correction is necessary to subtract that portion of the mass 28 peak which results from the cracking pattern of the CO_2 , i.e. 19.3% of the CO_2 peak at 470°C . Substituting the appropriate values into

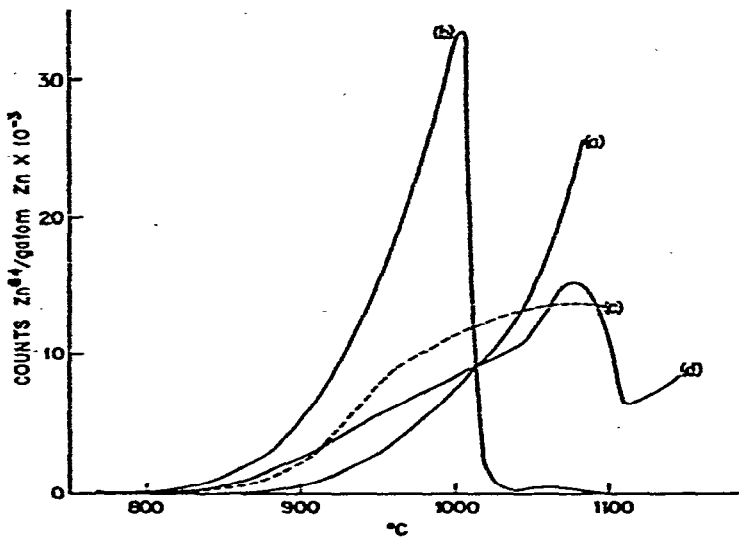


Fig. 5. EGA plots for various materials containing Zn. 100°C/h; mass 64. (a) ZnO; (b) ZnFe₂O₄; (c) Ni_{0.61}Zn_{0.37}CO_{0.02}Fe_{2.00}O₄; (d) Mn_{0.52}Zn_{0.43}Fe_{2.05}O₄.

eqn. (2) gives a value of $F_{CO} = 5.22 \times 10^{-7}$ g_{CO}/count. This enhanced sensitivity relative to CO₂ is at least partly due to less cracking of the parent molecule. Similarly, factors could be determined for other gases, e.g. H₂O, NH₃, O₂, etc. by choice of suitable and well defined compounds.

Zinc and oxygen loss from ferrites The close proximity of the sample and mass spectrometer enables the study of vapors which would otherwise have condensed prior to detection. Figure 5 shows such an example. The loss of Zn during the firing cycle of ferrites is a problem of considerable concern. The extent is inversely dependent upon the partial pressure of oxygen since it proceeds through a dissociative mechanism according to eqn. (7)¹.



Vacuum will therefore greatly exaggerate the loss. For ZnO there is a small loss of Zn (<0.3%) but not of O₂ that occurred in the range of 600–700°C which is attributed to the non-stoichiometric nature¹¹ of ZnO, i.e., Zn_{1+x}O. This early loss is not evident for any of the ferrites studied.

Except for this nonstoichiometric amount, the loss of Zn occurs more readily from ferrites than from ZnO. The ready reduction of trivalent iron provides an additional means of charge compensation for the loss of Zn from ferrites. The rate will naturally depend upon the surface area, diffusion rate and vacancy concentration of the sample. Admittedly, the surface areas of the materials shown in Fig. 5 are not known but it is not expected that they would vary sufficiently to change the qualitative picture. Initial or final surface areas would be of little use since the surface area undoubtedly changes during the heating-decomposition cycle. Near equilibrium

vacancy concentrations will very likely be established by the relatively slow heating in vacuum.

The weight lost by the ZnFe_2O_4 sample (39%) is in good agreement with that predicted from eqn. (8) (34%).



A calibration similar to that done earlier for CO_2 and CO gives a value of $8 \times 10^{-5} g_{\text{Zn}}/\text{count}$ for the mass 64 peak. The natural abundance of this isotope is the highest, about 49%. The reduced sensitivity compared with CO_2 and CO is not unreasonable considering the much greater tendency for $\text{Zn}_{(g)}$ to condense.

There are major peaks in O_2 loss corresponding to the loss of Zn as predicted by eqn. (8). However, there are considerably smaller but clearly evident losses of O_2 at lower temperatures of 500–800°C. These probably arise from excess O_2 and cation vacancies generally present in calcined ferrites. A direct correspondence between the loss of O_2 and Zn is not attempted because of the complications due to the concomitant reduction of trivalent iron.

CONCLUSIONS

An apparatus is described which is capable of performing qualitative evolved gas analysis with a high degree of sensitivity over the temperature range of 100–1300°C.

Semiquantitative data can be obtained using simple procedures based on the use of the thermal decomposition of suitable well defined compounds as standards. This was illustrated for CO_2 and CO using CaCO_3 and CaC_2O_4 as standards.

The apparatus is suitable for the study of readily condensable gases as well as permanent gases. This was illustrated with a brief study of the loss of Zn from various ferrites.

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