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APPLICATIONS OF EVOLVED GAS ANALYSIS TO THE STUDY OF INORGANIC MATERIALS AND PROCESSES

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The value and versatility of evolved gas analysis (EGA) are described by the use of selected recent examples. Three particular attributes of EGA methods are stressed. The first, specificity, reveals the frequent necessity of using EGA to substantiate conclusions based upon other thermal analytical techniques e.g. thermogravimetry (TG) or differential thermal analysis (DTA). To this end, the weaknesses of other thermal analytical techniques for the analysis of asbestos is reveladed by EGA. However, because of EGA's specificity it could be used for this purpose. Second, sensitivity, is demonstrated by use of mass spectrographic EGA techniques to study the kinetics of the early stages for the thermal decomposition of InP. This is further illustrated by qualitative assessments of the effects of various films in contact with the InP upon its thermal decomposition. A third advantage of EGA, insensitivity to experimental perturbations arising from an external magnetic field gradient, allows for its use to study the effects of such field gradients with less ambiguity than occurs with TG or DTA. This is shown for studies of the reduction of NiO, Fe_2O_3, and Co_3O_4 by H_2.

Thermal analysis to most scientists suggests thermogravimetry /TG/ and differential thermal analysis /DTA/. These, of course, have been the principal and traditional techniques; however, the spectrum of methods has expanded dramatically in recent years. Evolved gas analysis /EGA/, primarily involving mass spectrometry; has proven particularly useful. This paper has a missionary purpose and is intended to illustrate the power and versatility of EGA by means of a brief review of some selected examples for the author's recent work.

Three attributes or advantages of EGA are stressed. These are 1/ specificity - an ability to distinguish the actual nature of the material evolved, not just the change in weight or temperature; 2/ high sensitivity particularly using mass spectrometry; and 3/ freedom from experimental perturbations induced by external magnetic field gradients. The latter advantage is seldom a factor but can become extremely important in studying the effects of such fields. One of these factors is illustrated by each of the following sections.

EXPERIMENTAL AND RESULTS

Routine determination of the mineral composition of asbestos deposits[1]

Both TG and DTA have been suggested as possible analytical techniques for the evaluation of the content of the six common minerals present in asbestos deposits [2]. These minerals are chrysotile $Mg_3Si_2O_5(OH)_4$, brucite $Mg(OH)_2$, calcite $CaCO_3$, dolomite $CaMg(CO_3)_2$, talc $Mg_3H_2(SiO_3)_4$, and magnesite $MgCO_3$. A TG round robin, under the auspices of The Quebec Asbestos Manufacturers Association, was initiated in the early 1970's in an effort to demonstrate that these minerals decompose at different temperatures and hence such a mixture could be analyzed successfully by conventional thermogravimetric analysis.

The initial results [2] suggested a scheme of analysis represented by Fig. 1 in which the decomposition zones indicated are the averages derived from that round robin. Based upon the application of such a template to the TG or DTG curves it was possible to calculate the percentages of each mineral in a wide variety of asbestos deposits. Due to the reversibility of many of the decompositions, there is obvious concern that the temperature zones of decompositions are significantly influenced by the partial pressure of the products, e.g., $\underline{P}_{CO_2}$ for calcite and $\underline{P}_{H_2O}$ for brucite.

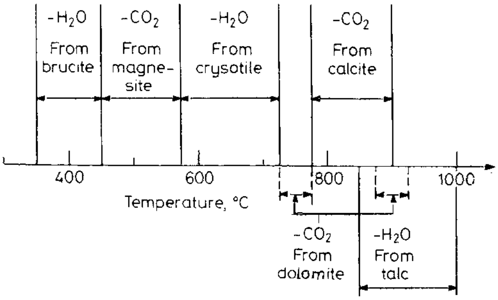

Fig. 1. Zones of thermal decomposition of various components of asbestos deposits [2]

Figures 2 and 3[1] which compose the EGA, TG, and derivative DTG curves for several asbestos deposits clearly show the seriousness of this problem. The difference in brucite contents between the two materials is clearly evident in both the TG/DTG and EGA results. The temperature of the DTG peak corresponds well with the window suggested in Fig. 1. But, the reversible

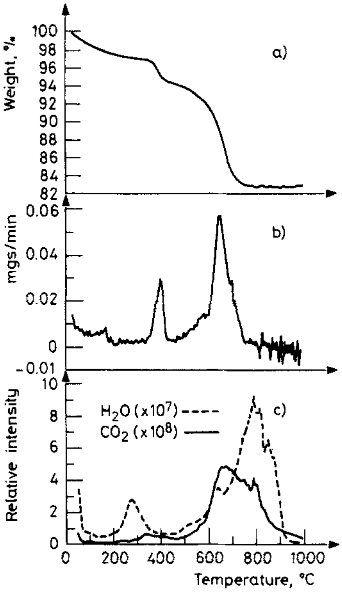

Fig. 2. Thermal decomposition of asbestos A.

a/ TG at 5•degree min^{-1} in air, 10.3 mg.

b/ DTG of above.

c/ EGA at 5 degree min^{-1}, ~10^{-7} torr, 14.9 mg.

nature of that decomposition leads to a shift in vacuum to considerably lower temperature. This, however, only serves to enhance the separation between the brucite and chrysotile decompositions in the EGA. The higher temperature dehydrations of chrysotile and talc appear to merge and be more drawn out in the EGA results. This not only complicates their resolution, but also, leads to substantial overlap with the various carbonate decompositions.

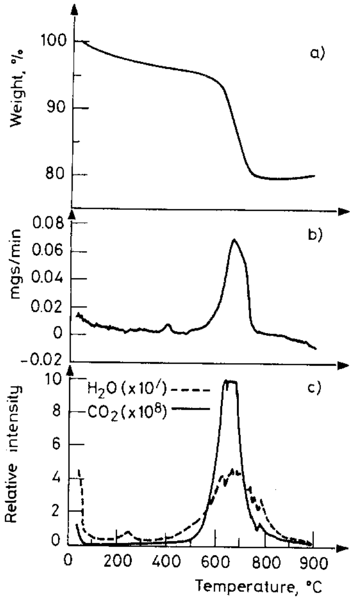

Fig. 3. Thermal decomposition of asbestos B.
a/ TG at 5'degree min^{-1} in air, 10.0 mg.
b/ DTG of above.
c/ EGA at 5 degree min^{-1}, $\sim 10^{-7}$ torr, 13.3 mg.

Although the EGA profiles of the high temperature evaluation of water for the two samples are quite similar, there are notable differences in the CO_2 evolution profiles. Sample B /Fig. 3/ shows a strong narrow peak around 650°, probably arising from calcite decomposition. This weight loss very closely corresponds with the chrysotile decomposition. The calcite temperature occurs at a lower temperature than implied in Fig. 1. This again is a result of the reversibility or dependence upon

$\underline{P}_{CO_2}$. The local build up of CO_2 is less in the vacuum or flowing air of this work than that used as a basis for Fig. 1.

The EGA curve for CO_2 in sample A /Fig. 2/ is distinctly different with the principal evolution of CO_2 at 800°. It is much broader and probably includes unresolved components from both calcite and dolomite. There is a small peak near 350° which is probably due to the decomposition of magnesite at low $\underline{P}_{CO_2}$. It must be remembered, when comparing the EGA curves with the DTG curves, that the EGA curve for CO_2 has been magnified /x10/ relative to the H_2O and the relative sensititivites of the mass spectrometer to the two gases are undoubtably somewhat different. These factors in addition to the differences in molecular weights precludes a simple addition of the two EGA curves in an effort to reproduce the DTG curve.

The ability of EGA to distinguish between the loss of H_2O and CO_2 greatly enhances the ability of this technique to solve the problem associated with overlap of the various decompositions. Quantitative EGA would clearly be more likely to yield the true composition. However, more specifically defining the atmosphere for the TG experiments would certainly improve the precision or reproducibility of those results and might even make a successful resolution of the reactions possible. One approach to this is the use of self-generated atmospheres to quickly provide an ambient of nearly pure decomposition products. Alternatively, one could provide a well defined flowing atmosphere, e.g., CO_2 saturated with H_2O at some established temperature that would hopefully provide an atmosphere in which the presence or absence of the small amount of decomposition products was irrelevant.

Thermal decomposition of InP and related materials [3-5]

Polished substrates of InP are used for the epitaxial growth of numerous microwave and optoelectric devices. Temperatures during processing sometimes rise above the decomposition threshold of InP for short times. Incongruent vaporization of phosphorous occurs above ~630K [6] resulting in deleterious free In at the surface. Obviously, knowledge of the early stages of the loss of phosphorous from InP is of considerable technological importance. The great sensitivity of the mass spectrometer allows one to study the decomposition at very small fractions reacted, α, i.e., $\alpha < 0.01$. This analytical technique coupled with the kinetic analysis method developed by Ozawa [7] permits determination of the Arrhenius parameters associated with this early stage of decomposition.

The Ozawa method of analysis requires values of temperature at selected values of α at several heating rates. The activation energy /$\underline{E}$/ is derived from the slope of a plot of the log of the heating rate versus reciprocal temperature for the selected values of α. A set of typical experimental data /20 degree min^{-1}/ is shown in Fig. 4. The decomposition is monitored by following the intensity of the P_2 evolution at several values of amplification [3]. The value of α is determined by comparing the area under the curve up to the selected point with the area for the total decomposition after applying the appropriate amplification factor. Arriving at a preselected value of α would require an impractical iterative process using the manual planimeter. Therefore values of α were calculated at conveniently selected points, e.g. the 9 arrows in Fig. 4, and a plot of log α $\underline{\text{vs}}$. temperature proved linear. The temperatures associated with the desired values of α could then be ob-

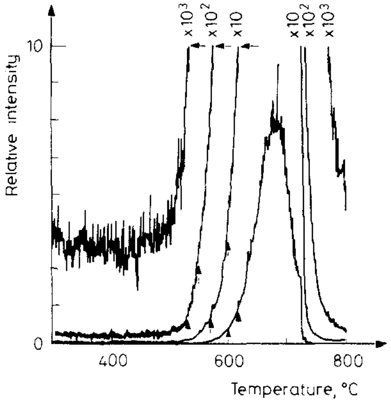

Fig. 4. Relative intensity of P_2 $\underline{\text{vs}}$. temperature for 0.95 mg of InP heated at 20 degree min^{-1} in vacuum /5×10^{-8}torr/. Arrows represent points of analysis [3].

tained by interpolation. Using this approach, the values of temperature at six selected values of α /$\leq$ 0.10/ were determined for five heating rates /0.5-20 degree min^{-1}/. These values are given in Table 1 along with the values of the Arrhenius parameters derived using the Ozawa method. The calculated Arrhenius parameters are remarkably consistent yielding average values of $\underline{E}$=294.7 kJ.mole^{-1} and log $\underline{A}$=13.85 sec^{-1}. Numerical analysis of the experimental data over the whole range of decomposition using other methods of numerical analysis gave consistant but more variable results and suggested that the reaction followed a pseudo first order rate law [3]. This latter result is coupled with the Arrhenius parameters enables one to calculate the curves shown in Fig. 5. Plots such as these are of value to the technologist and represented the goal of the study.

Table 1

Temperature as a function of fraction reacted for various heating rates and the Arrhenius parameters calculated by the Ozawa method [13]

Heating rate	Temperature, °C						
	α = 0.10	0.03	0.01	0.003	0.001	0.0003	
20	632.0	610.2	591.2	570.2	555.1	530.0	
10	617.5	594.3	573.7	551.0	530.4	507.6	
5	615.2	593.7	573.5	553.5	534.0	513.0	
1	574.5	555.5	538.5	519.5	502.5	483.5	
0.5	559.5	540.5	523.8	504.5	487.5	468.7	
$\underline{E}$(kJ/mole)	295.1	296.3	299.2	293.8	293.8	290.9	294.7 avg.
log($\underline{A}$ sec^{-1})	14.03	14.03	14.16	13.56	13.76	13.58	13.85 avg.

Related EGA studies have been performed which show the influences of various thin films upon the decomposition of III-IV

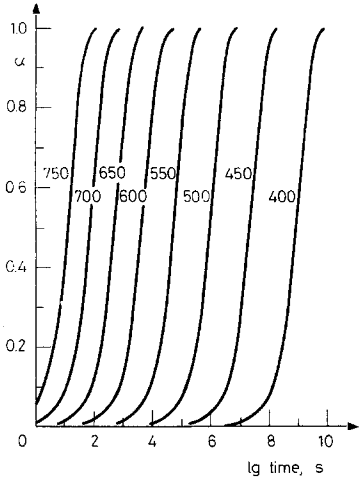

Fig. 5. Calculated isothermal decomposition curves for InP [3].

compounds. Gold electrodes on GaAs or /GaAl/As lead to premature evolution of As due to preferential dissolution of the Ga into Au [5,8]. On the other hand certain refractory films such as Al_2O_3, Si_3N_4, etc., have a protective influence and inhibit the decomposition [4]. Figure 6 shows examples of both effects. The InP is coated with Al_2O_3 on both sides but the edges are uncoated leading to the small decomposition peak at the same temperature as the uncoated sample.

Reduction of oxides by H_2 [9,10]

Gravimetric techniques have been used to measure the effect of an external magnetic field on the reduction of some transition metal oxides [11,12]. Several factors come to mind which would suggest uncertainties and possible ambiguities that might arise in such studies. The two major considerations are the development of "bulk" /or at least constant/ magnetic properties of the product and/or reactants and secondly, the possible movement of the individual particles or sample relative to the magnetic field gradient. Since the apparent weight of a highly magnetic sample in a strong field gradient is largely determined by the magnetic interactions, it would seem that gravimetric

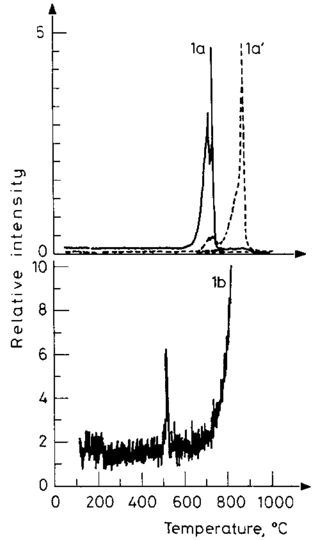

Fig. 6. EGA curves at 20 degree min^{-1}.

a/ P_2 evolution from uncoated InP/(InGa)As——.

a'/ P_2 evolution from coated InP/(InGa)As ---.

b/ As evolution from GaAs with an Au film.

studies of the rate must be subject to these uncertainties. For the case in which magnetic products are formed, e.g., Eq. 1,

$$\alpha - Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O \qquad (1)$$

the initial reduction proceeds with the formation of the oxygen deficient oxide which at some point leads to the precipitation of a reduced phase Fe_3O_4 or more likely a solid solution of the spinels, γ-Fe_2O_3 and Fe_3O_4. Because the reaction occurs well below 500° where FeO is unstable, the Fe_3O_4 probably reduced to Fe without intermediate phase formation but with the oxygen and possibly even the OH or H_2 contents of the hematite, spinel, and metal phases changing during the course of the reaction. In addition to these compositional variables there is the effect of particle size as the new phases undoubtedly start as superparamagnetic nuclei and do not reach "bulk" magnetic properties until some finite size of the order of 100Å.

Besides this question of the changing magnetic properties, there is the tendency of the particles to align themselves with the magnetic field. To the extent that the magnetic particles shift or rotate /even by twisting the hang down wire/, there will be perturbations induced upon the apparent weight. For these reasons an EGA technique based upon the rate of formation of H_2O would seem more unambiguous.

An apparatus was assembled which measured the dew point of the H_2 gas at atmospheric pressure after it had passed over the heated sample [13]. Results were compared with simultaneous TG measurements and found to have very close correspondence [9,14]. Typical results are shown in Fig. 7. Once having established

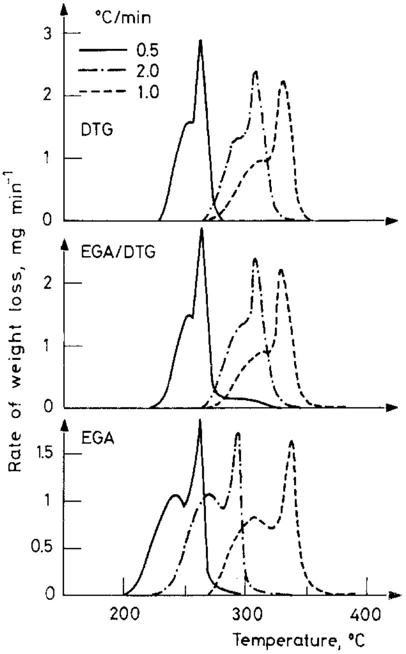

Fig. 7. Results for the reduction of NiO ($1.0\,m^2g^{-1}$) by H_2; (a) DTG curves 0.5 degree min^{-1}, 26.12 mg, -21.1 wt %, (X20) 2.0 degree min^{-1}, 27.08 mg, -21.3 wt %, (X5) 10 degree min^{-1}, 26.12 mg, -21.4 wt %, (X1) (b) Simultaneous EGA curves of above (c) EGA curves using the apparatus designed for work in a magnetic field 0.5 degree min^{-1}, 24.20 mg, -21.2 wt %, (X20) 2.0 degree min^{-1}, 24.69 mg, -21.4 wt %, (X5) 10 degree min^{-1}, 24.73 mg, -21.3 wt %, (X1).[9]

the reliability of this method it was possible to dispense with the gravimetric portion and modify the apparatus to function in a strong magnetic field. Dynamic temperature measurements were performed rather than isothermal studies because of their relative ease and speed. It was felt that they would quickly reveal any major differences in reaction rate induced by a magnetic field. Results are shown for Fe_2O_3 and Co_3O_4 in Figs. 8 and 9.

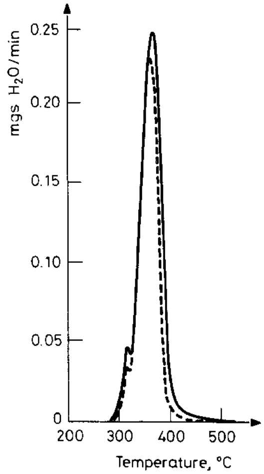

Fig. 8. EGA curves for the reduction of Fe_2O_3 (016 m^2g^{-1}) by H_2 at 10 degree min^{-1}; 5.26 mg, -34.8 wt %, 0 kOe —; 4.80 mg, -34.8 wt %, 7 kOe --- [10].

No major difference in the rate of the reduction in the strong magnetic field was obvious, however, dynamic experiments are less likely than isothermal measurements to detect the subtiles, smaller effects. The EGA technique, of course, is applicable as well to isothermal studies [15].

CONCLUSIONS

It should be obvious from the examples presented herein that EGA deserves greater usage. The ability to distinguish the specific nature of the gaseous product and the high sensitivity of some EGA techniques present a frequently unique capability. As the complexity of systems under investigation grows

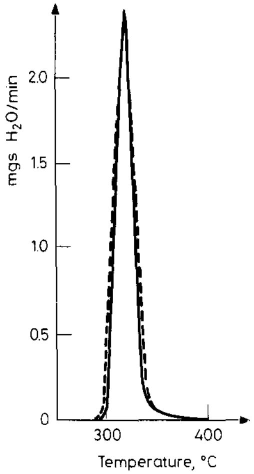

Fig. 9. EGA curves for the reduction of NiO (1.0 m^2g^{-1})by H_2 at 2 degree min^{-1} 25.61 mg, -21.2 wt %, 0 kOe ——; 24.69 mg, -21.2 wt %, 4 kOe --- [10].

or the demands for lower limits of detection increase, EGA will assume a more prominent role in thermal analysis.

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ZUSAMMENFASSUNG - Die Bedeutung und die Vielseitigkeit der EGA wird anhand ausgewählter neuerer Beispiele beschreiben. Drei besondere Merkmale der EGA-Methoden werden hervorgehoben. Die erste, die Spezifität, wird der häufigen Notwendigkeit zur Anwendung der EGA gerecht, um auf andere thermische Analysentechniken, z.B. auf TG oder DTA beruhende Schlussfolgerungen zu stützen. Dies wird demonstriert, indem gezeigt wird, dass die EGA die Unzulänglichkeiten anderer thermischer Verfahren zur Analyse von Asbest in Erscheinung treten lässt und infolge ihrer Spezifität für diesen Zweck geeignet ist. Das zweite Merkmal, die Empfindlichkeit, wird durch Anwendung der massenspektrographischen EGA-Technik zur Untersuchung des frühen Stadiums der thermischen Zersetzung von InP demonstriert. Dies wird weiter durch qualitative Beurteilung der Wirkungen von verschiedenen in Kontakt mit dem InP befindlichen Filmen auf dessen thermische Zersetzung illustriert. Ein dritter Vorteil der EGA is deren Unempfindlichkeit gegenüber von äusseren magnetischen Feldgradienten herrührenden experimentellen Störungen, wodurch diese Methode bei der Untersuchung der Wirkungen solcher Feldgradienten eindeutigere Ergebnisse als die TG oder DTA liefert. Dies wird anhand von Untersuchungen der Reduktion von NiO, Fe_2O_3 und Co_3O_4 mit H_2 gezeigt.

Резюме - На избранных примерах показана ценность и многосторонность метода анализа выделяющегося газа /АВГ/. Сделан упор на три исключительные особенности метода АВГ. Во первых, специфичность метода, показывающая частую необходимость использования метода АВГ для подтверждения заключений, сделанных на основе других термических аналитических методов: например, ТГ или ДТА К тому же, слабость других термических аналитических методов для анализа асбестов по сравнению с АВГ. Поэтому для этой цели и может быть использован метод АВГ. Во вторых - чувствительность, показанная использованием масс-спектрографических методов АВГ для изучения кинетики ранних стадий термического разложения InP. Это и дальше иллюстрируется качественной оценкой влияния различных пленок, находящихся в контакте с In P при его термическом разложении. Третьим преимуществом метода АВГ является нечувствительность его к экспериментальным помехам, возникающим вследствии проявления градиента внешнего магнитного поля. Этот факт позволяет исследовать влияние этого эффекта с гораздо меньшей неопределенностью по сравнению с методами ТГ и ДТА. Все это представлено при изучении реакции восстановления водородом окислов двухвалентного никеля, трехвалентных железа и кобальта.