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EARTH SCIENCES APPLICATIONS OF EVOLVED GAS ANALYSIS: A REVIEW

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ABSTRACT

Areas of application of EGA in the assessment of geological materials are reviewed, and illustrated by data obtained using thermal analysis systems employing a mass spectrometer and non-dispersive infrared detectors.

INTRODUCTION

Thermoanalytical methods such as differential thermal analysis (DTA) and thermogravimetry (TG) have been used extensively to characterize geological materials and to evaluate these for various applications. In spite of the greater degree of analytical performance potentially available from evolved gas analysis (EGA), this technique has by no means achieved the same degree of use. The most common volatiles evolved on heating geological materials are water, carbon dioxide and sulphur dioxide. Analysis systems employing specific detectors are thus practical and non-dispersive infrared (NDIR) detectors are fully quantitative for these volatiles. However, other volatiles such as oxygen, hydrogen and carbon monoxide are often encountered and the analytical flexibility of a mass spectrometer (MS) is then required. Using either NDIR or MS, mineral detection limits are orders of magnitude lower than for X-ray diffraction. This short review covers a number of actual and potential applications of EGA in the earth sciences. Examples are mainly taken from work by the present authors using thermal analysis systems employing NDIR detectors [1] and MS [2], these being supplemented by data from the literature.

QUANTITATIVE ANALYSIS OF MINERAL MIXTURES

Only rarely can X-ray diffraction (XRD) detect minerals present in natural samples below the 2-3% level, whereas EGA has the potential for determining certain minerals well below XRD detection limits. This has important implications for studies of oil-reservoir sandstones and argillaceous strata for low-level radioactive waste disposal, where the presence of small amounts of labile mineral phases may be significant not only for unravelling diagenetic events, but for practical reasons such as their effect on porosity (clays), cementation (carbonates) and their buffering capacity under anaerobic conditions (sulphides). Work on dilution sequences of carbonate minerals in alumina using an NDIR detector [3] has shown that it is possible to both identify and quantify amounts of calcite, magnesite and strontianite down to 50 ppm.

Fig. 1 shows volatile evolution profiles for a brick clay rich in organic matter obtained using an EGA system employing NDIR detectors. Amounts of volatiles evolved (and hence amounts of original mineral phases) can be determined from peak areas either by empirical calculation [1] or by

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comparison with volatile evolution profiles from selected chemical compounds. Among those found to be most suitable in routine use are sodium bicarbonate (H_2O and CO_2), sodium dithionate (H_2O and SO_2) and magnesium oxalate (H_2O , CO and CO_2). Much work needs to be done in the development of EGA standards; the production of dilute standards is by no means straightforward, and many carbonates have been found to deteriorate by hydrolysis on long storage.

Fig. 2 shows volatile evolution profiles of the same clay obtained using an EGA system employing MS. It is encouraging to note that even in this complex mineral assemblage - and an entirely different sensing system, flow conditions, sample size and environment - the volatile evolution profiles are virtually identical with those determined using the NDIR detectors. Combustion reactions such as the one figured are especially prone to modification by self-generated atmospheres, purging efficiencies and catalylitic effects of platinum parts in the instrument. The MS trace for SO_2 in Fig. 2 demonstrates, in addition, the high sensitivity that can be attained, and this can be increased still further by using a jet separator at the interface to the MS [2]. Preliminary work on detection limits for CO_2 by the present authors implies values <10 ppm are possible.

The benefit of conducting EGA - even in qualitative mode - simultaneously with TG is illustrated by Fig.3. The TG curve shows two weight losses corresponding to the dehydroxylation of brucite [$Mg(OH)_2$] and dissociation of calcite, respectively. The water evolution profile shows an additional peak at 648°C due to dehydroxylation of chrysotile (an asbestiform Mg-silicate). Measurement of the weight loss on the TG curve between the temperature limits indicated by this water evolution peak suggests a maximum amount of 2% chrysotile, which would otherwise have remained undetected. The ability of MS to simultaneously monitor all possible volatiles, rather than those expected, may thus may reveal unsuspected thermal events.

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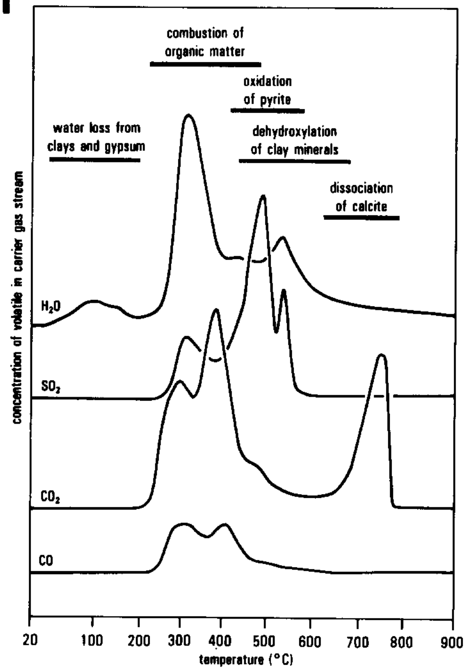

Fig. 1. EGA(NDIR) of brick clay, Bedfordshire, UK. Sample weight 100 mg, heating rate 15°C/min., flowing air.

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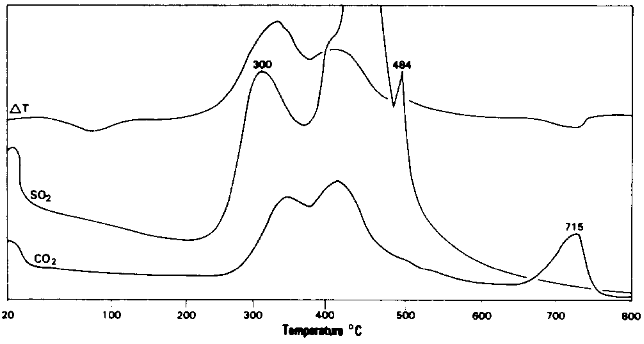

Fig. 2. EGA(MS) of brick clay, Bedfordshire, UK. Sample weight 20 mg, heating rate 10°C/min., flowing air.

FUNDAMENTAL STUDIES OF MINERAL THERMAL DECOMPOSITION PROCESSES

Although DTA-TG may often be sufficient for mechanistic studies of mineral thermal decomposition processes, the volatile release from complex minerals containing many anion groups requires simultaneous monitoring of several gases for an unambiguous interpretation of the degadation pathway. In the mineral leadhillite $[Pb_4SO_4(CO_3)_2(OH)_2]$, for example, CO_2 is released in two distinct stages between 300° and 500°C [4] in reactions involving formation of a series of Pb-oxysalt intermediates. NDIR detectors were sufficient to follow these reactions and provide quantitative data for CO_2 and H_2O release. In the related mineral caledonite $[Pb_5Cu_2(SO_4)_3(CO_3)(OH)_6]$, CO_2 and H_2O were released in a single reaction between 300° and 400°C [5], but MS showed multistage O_2 evolution above 800°C due to reactions involving earlier-formed Cu-oxide intermediates and dissociation of expelled SO_3.

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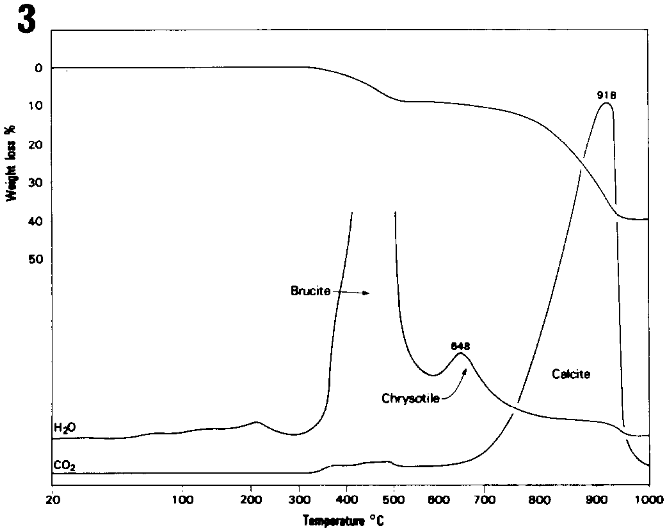

Fig. 3. EGA(MS) of brucite-marble, Wakefield, Canada. Sample weight 86 mg, heating rate 30°C/ min., flowing argon.

EGA systems employing both CO_2 and CO detectors are essential for studying decomposition mechanisms of Fe-bearing carbonate minerals. The TG curve of ankerite [$Ca(Mg,Fe)(CO_3)_2$] shows that it breaks down in at least three reactions with loss of CO_2 [6]; CO is also evolved during the first two reactions, mainly due to reduction of CO_2 by Fe(II)-bearing intermediates of the decomposition. Such reactions are controlled largely by sample-generated atmospheres. Fig. 4 shows simultaneous TA-MS curves in argon for siderite [$FeCO_3$] ground to different particle sizes. The overall reaction in both cases is $3FeCO_3 \rightarrow Fe_3O_4 + 2CO_2 + CO$. Initially, FeO is formed due to the reaction $FeCO_3 \rightarrow FeO + CO_2$. Some of the earlier-formed FeO may disproportionate to Fe and Fe_3O_4 exothermically [7], this reaction being responsible for the interruption to the sharp endothermic reaction on the DTA curve for the freshly ground, coarser sample in Fig. 4. FeO (and Fe) reduce the sample-generated CO_2 to CO, being in turn oxidized to Fe_3O_4. In the more finely-ground sample, internal CO_2 pressures are lower and the separate components of the decomposition are not defined on either TA or MS curves. Unpublished work on a series of ground siderites by the present authors has shown that the evolved CO : CO_2 ratio increases with increase in particle size, the longer diffusion path in the coarser samples allowing greater contact of the CO with Fe(II).

Similar redox reactions occur during thermal decomposition of Fe(II)-bearing silicates. The amount of hydroxyl water evolved is often appreciably less than predicted from the structural formula due to reduction of a significant proportion of this to hydrogen by Fe(II) (Fig.5). The same effect has been demonstrated for an iron-bearing member of the chlorite group of minerals [2].

FURTHER APPLICATIONS AND POTENTIAL APPLICATIONS OF EGA

EGA profiles (by MS) have been used to characterize volcanic ashes from different environments [8] and have also been used to investigate crystallization behaviour of volcanic glasses [9]. It has been shown recently [10] that hydroxyl water condensates from clays and shales contain trace

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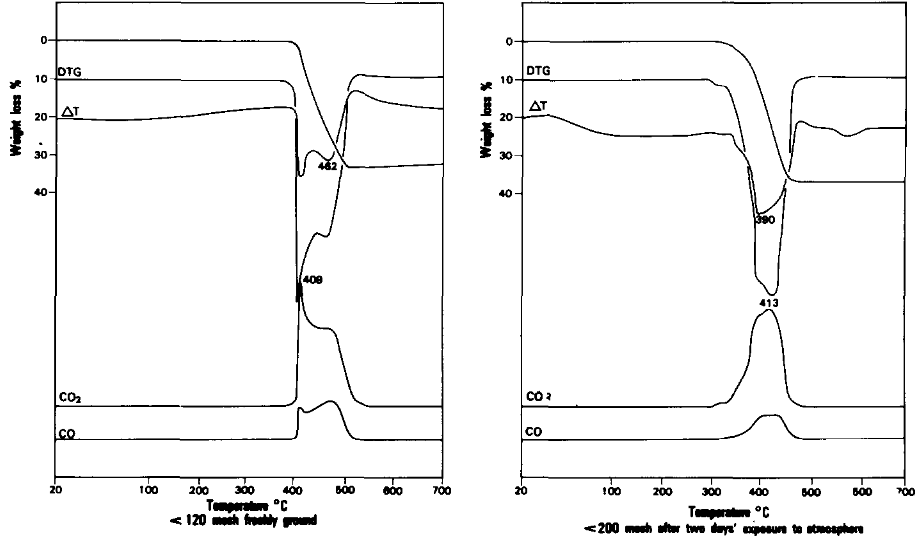

Fig. 4. EGA(MS) of siderite, Ivigtut, Greenland.Sample weight 19 mg, heating rate 15°C/min., flowing argon.

amounts of elements such as F, Cl, B and Br, together with oxides of nitrogen and sulphur. Measurement of the temperature-release patterns of these volatiles may link them to individual mineralogical phases and thus provide information on the geological history of these fine-grained materials. In the assessment of metallic minerals, the analysis of effluent gases provides essential information on the pre-reduction behaviour of hematite and chromite ores and the roasting properties of non-ferrous (sulphide) ores. For non-metallic minerals, simultaneous TG-EGA studies are invaluable for quantitative analysis of talc, graphite and kaolin raw materials and products from separation trials on these. EGA can also be used to quantify impurities such as carbonates and sulphides in ceramic clays that may cause problems during firing.

Kinetics of the pyrolysis of oil shales can be obtained from measurement, by MS, of rates of evolution of carbon oxides, hydrogen and hydrocarbons [11]. EGA(MS) has also been used to investigate the thermal processes taking place during brown coal pyrolysis [12]. EGA(NDIR) is a potential tool for distinguishing between and quantifying the various forms of sulphur in coals [13] - an important area in view of the increasing use of lower-grade coals and consequently greater likely environmental pollution.

CONCLUSIONS

It is likely that coupled EGA or EGA alone will be used more widely in the earth sciences as suitable, reliable instruments become more readily available.Those employing MS offer versatility, but if only one or two volatiles are to be investigated then a system with NDIR detectors is more cost-effective. Newer combinations of thermoanalytical systems employing Fourier transform infrared analysis may well achieve prominence in the future, especially for investigations of coals and oil-bearing strata.

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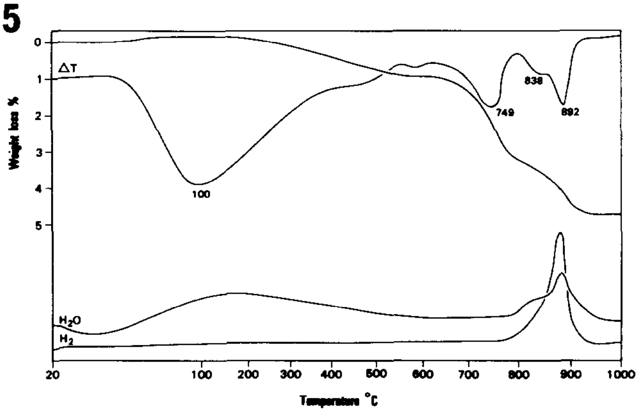

Fig. 5. EGA(MS) of grunerite [$(Fe,Mg)_7Si_8O_{22}(OH)_2$], Penge, South Africa. Sample weight 41 mg, heating rate 30°C/min., flowing argon.

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