Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 393–401

TG EVOLVED GAS ANALYSIS USING ATD SAMPLE TUBES

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Abstract

A new variation of off-line TG evolved gas analysis is reported here. Gas collection is done by inserting sample tubes filled with a suitable adsorbent, into the exhaust from the TG instrument. The following gas analysis is carried out by placing the sample tubes into a commercial thermal desorption unit which is coupled to a GC/MS. In this way, both a chromatographic separation of components as well as a mass spectral identification are obtained. Two examples from the analysis of production chemicals demonstrate the usefulness of this approach.

Keywords: autothermal desorption unit, gas sample tubes, off-line evolved gas analysis, production chemicals, thermogravimetric analysis

Introduction

Thermogravimetric (TG) analysis is a well known and much used technique in a wide variety of fields. It provides information about different thermophysical processes like evaporation, decomposition and degradation that take place in samples during heating [1]. For relatively simple and well known samples it might be possible to associate a single mass loss with a specific thermal process. For more complex (or little known) samples the interpretation of TG curves is often much more difficult. In such cases, evolved gas analysis can contribute to the elucidation.

TG analysis followed by evolved gas analysis using GC, FTIR and MS have been reported. This can be carried out on-line, that is the evolved gas from the TG analyser is directly fed to a second instrument like MS or FTIR [2–5]. It can also be carried out off-line, in which case the gas is either bubbled through a solution and then recovered for further analysis or captured by an adsorbing solid prior to desorption and injection into a GC for analysis [6, 7].

A new variation of off-line evolved gas analysis is reported here which utilises sample tubes filled with a suitable adsorbent for collecting the gas. The two examples which demonstrate the validity of this approach include the identification of unknown components in mixtures of chemicals and the identification of decomposition products from chemicals used in oil and gas processing. The advantages and disadvantages of the experimental set-up are discussed.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Coupling of sample tube to TG apparatus and experimental conditions

Statoil has a Perkin Elmer TGA7. The instrument is designed in such a way that a Pyrex furnace tube surrounds the oven and the sample. Approximately 10 cm below the oven there is an opening in the Pyrex tube which constitutes the exhaust outlet into a plastic tube. This exhaust port was moved up to the level of the oven. The sample tube was then simply inserted into the plastic tube at this exhaust. In this way, the length from the point of generation of the gas to the point of gas collection was considerably shortened and thus the condensation of evolved gases was largely avoided.

The liquid samples to be studied were heated in the TGA7 until the mass loss curves indicated complete evaporation. The purge gas used was helium of 99.999% purity (supplied by Hydrogas AS) and the most commonly used heating rate was 10 K min^{-1}. The sample mass was between 5–10 mg and the gas flow rate in the TGA7 was 30 ml min^{-1}. The volatile components were carried with the purge gas through the sample tube after which the tube was disconnected from the TGA7 and reconnected to the ATD-400 unit for desorption and analysis. Blank runs (no sample in the TGA7 during heating) were run in between samples in order to check the level of cross contamination.

Thermal desorption unit

A Perkin Elmer ATD-400 was the thermal desorption unit used for analysis of the collected TG exhaust gas. This is a two-stage thermal desorber, which means that the analytes are desorbed from the sample tube and concentrated in a smaller electrically cooled cold trap filled with an adsorbent, in this case Tenax TA (60/80 mesh). The cold trap is then heated to release the analytes to the GC/MS as narrow bands. The sample tubes were made of stainless steel and were also filled with 60/80 mesh Tenax TA. The tubes were heated under flowing helium at 230°C for transfer of the analytes to the cold trap. The cold trap was then heated at 5°C from 10–230°C for the transfer of analytes to the GC column.

GC/MS

The desorbed analytes were transferred through a heated transferline (fused silica tubing) to a Crompack CP WAX 52 CB (30 m×0.25 mm, 0.5 μm film thickness) capillary column in the GC/MS for separation. The GC was an AutoSystem GC from Perkin Elmer, with a Turbomass mass spectrometer, also delivered from Perkin Elmer. The heating program was as follows: hold 45°C for 2 min; ramp 5 K min^{-1} to 100°C; ramp 10 K min^{-1} to 230°C and hold for 10 min.

Results and discussion

Identification of solvents in production chemicals

Statoil uses a range of chemicals for the production of oil and gas. When qualifying or evaluating chemicals in the laboratory it is sometimes necessary to know their exact chemical composition. Because the production chemicals in general are complex mixtures, a direct GC/MS-analysis is often not advisable. Furthermore, the chemical data sheet that is available for every chemical is often an incomplete description. Firstly, the exact amounts of the various components are generally not specified. For instance, it is usual to find information like 60–100% of component 1 and less than 10% of component 2. From an analyst's point of view this is rather unsatisfactory! Secondly, there is no requirement to state the exact chemical nature of a component either. This then means that the analyst is faced with two analysis problems: the fractionation of the mixture followed by the analysis of the different fractions.

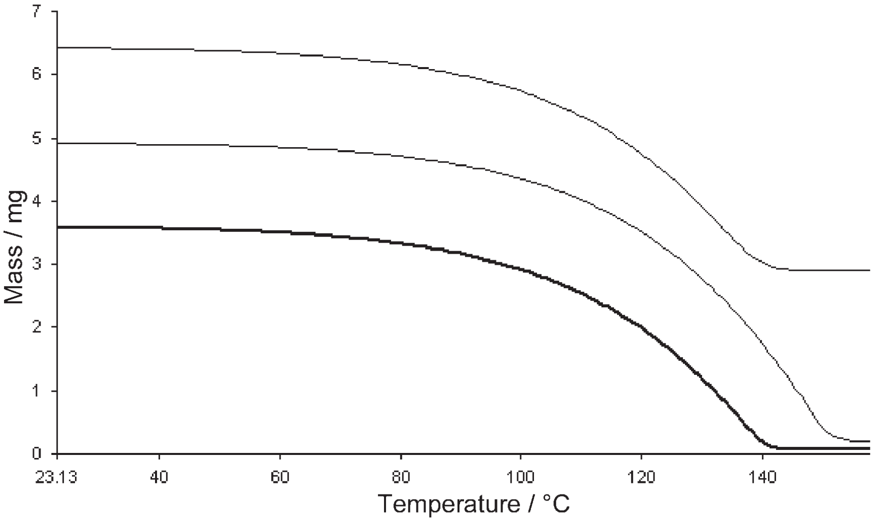

Fig. 1a TG mass loss curves of the three production chemicals; top curve: chemical B, middle curve: chemical C and bottom curve: chemical A

It has been reported that TG can be used to perform 'simulated distillations' [8].

An example is shown below in which this type of distillation in combination with evolved gas analysis can help to solve an analysis problem of the type described above.

According to the chemical data sheets the three production chemicals A, B and C contain an alkyl acetate as solvent. It was of interest to find out what alkyl acetate this was, how much of it was present in each case and if it was the same alkyl acetate in all three chemicals. The following approach was chosen: the three samples were heated, one by one, in the TGA7 until the mass loss curves showed a stable mass. The

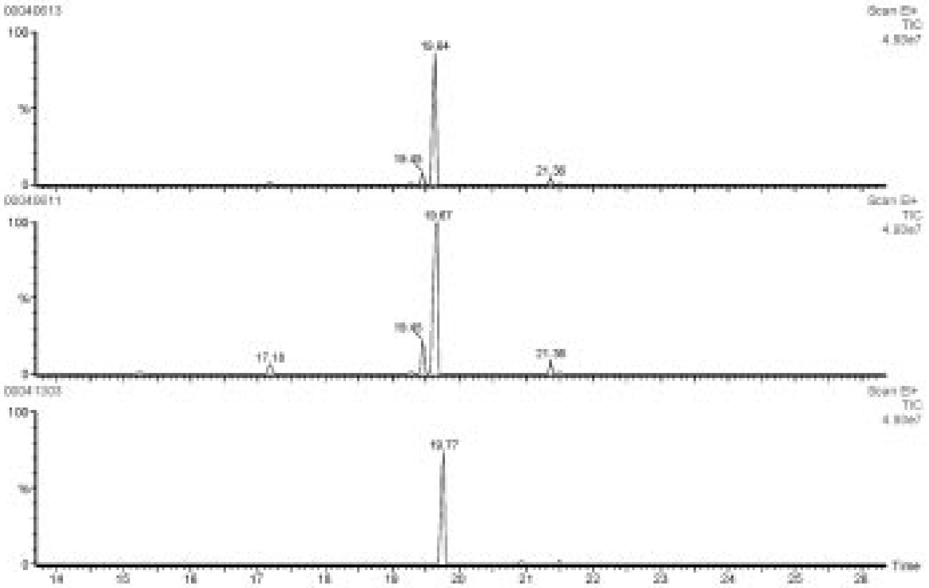

Fig. 1b Gas chromatograms of the TG evolved gas from the three production chemicals. Top: chemical A, middle: chemical B and bottom: chemical C

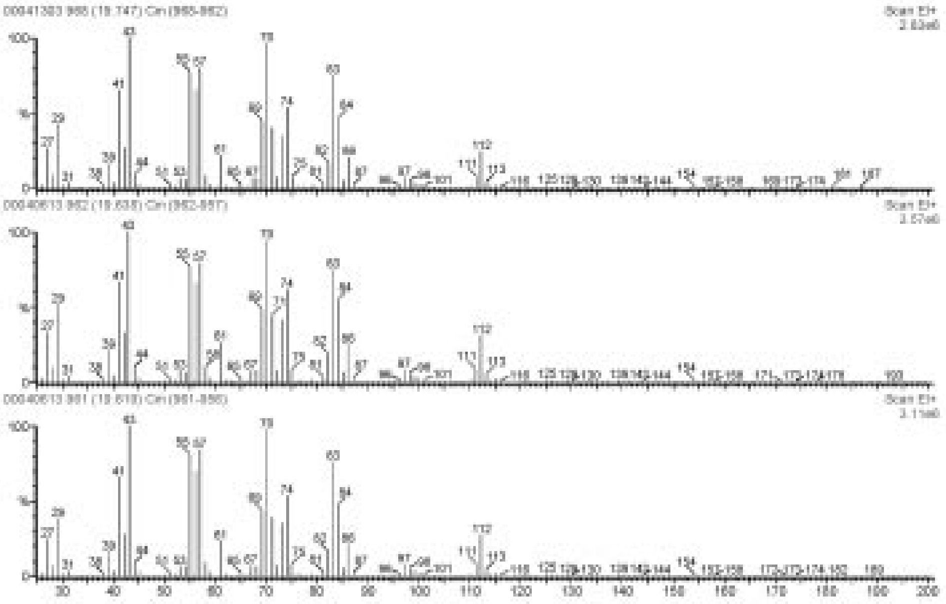

Fig. 1c Mass spectra of the main GC peak from each of the chromatograms shown in Fig. 1b, in the same sequence as in Fig. 1b

curves are shown in Fig. 1a, and data extracted from these curves are given in Table 1. It is seen that the mass change starts at around 50°C in all three cases and ends at around 150°C. Only chemical C has a slightly higher end point of mass loss which is also reflected in the higher T_{max} value (taken from the first derivative of the curve). The mass losses up to 150°C vary for the 3 chemicals. This is not surprising as the chemicals are designed to serve different purposes and thus are composed differently. Furthermore, the mass losses also indicate that the chemicals consist of at least one more component which evaporates at higher temperatures. It is concluded that heating of the chemicals in the TGA7 has lead to the distillation of parts of the samples and thus to a fractionation. The T_{max} values indicate that chemicals A and B have very similar boiling points and that all 3 chemicals boil in the same temperature region.

Table 1 TG data for the 3 production chemicals A, B and C

Data	Chemical A	Chemical B	Chemical C
T_{max}/°C	136	133	146
Mass loss/%	97.8	54.7	96.1

Evolved gas analysis was carried out as described above. The 3 gas chromatograms are shown in Fig. 1b. They contain one major peak for each gas sample with very similar retention times (19.64, 19.67 and 19.77 min for chemicals A, B and C, respectively). The corresponding mass spectra are shown in Fig. 1c. They are basically identical and could be identified by a search in Wiley's library of mass spectra (available software). The compound of interest is *n*-octyl acetate, or more generally speaking an alkyl acetate, as stated on the chemical datasheet. The other peaks in the chromatograms are carryovers from previous TG analysis. This shows the impor-

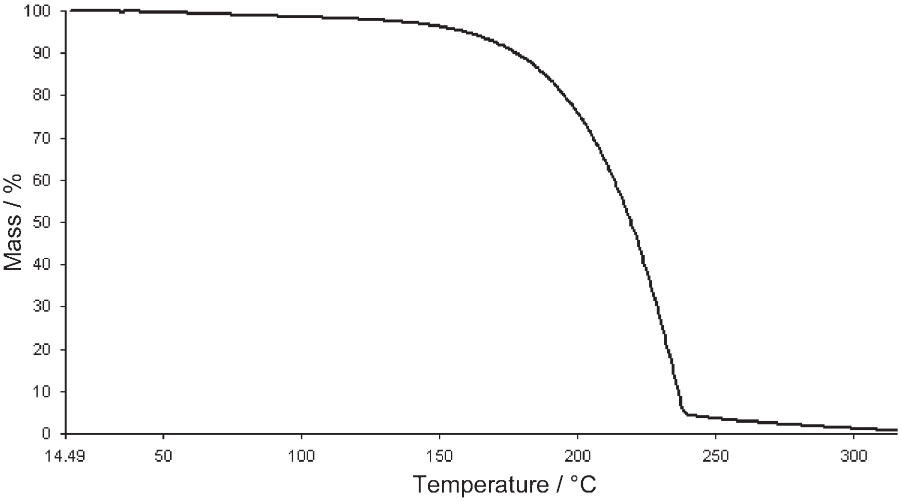

Fig. 2a TG mass loss curve of TEG

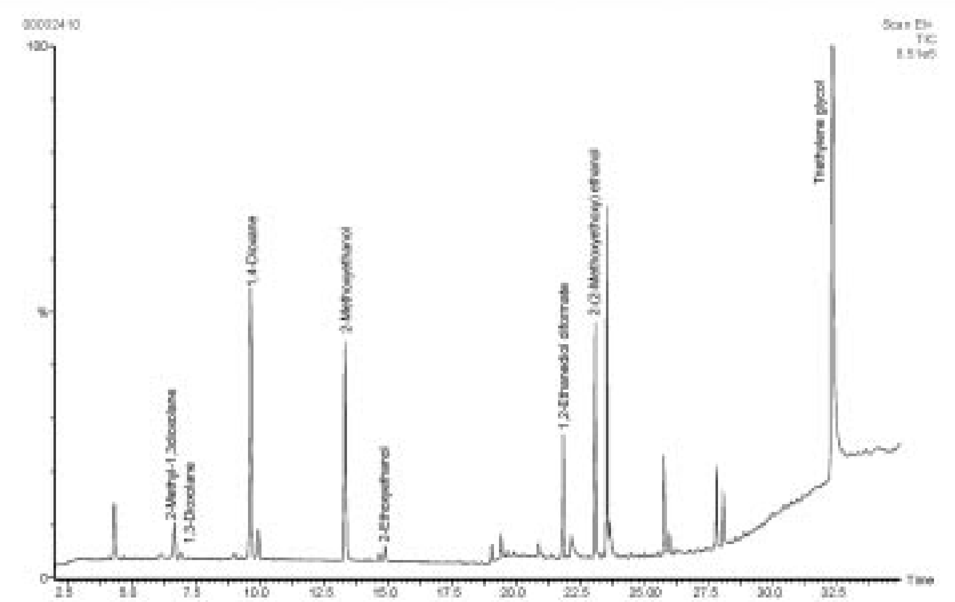

Fig. 2b Gas chromatogram of the TG evolved gas from TEG

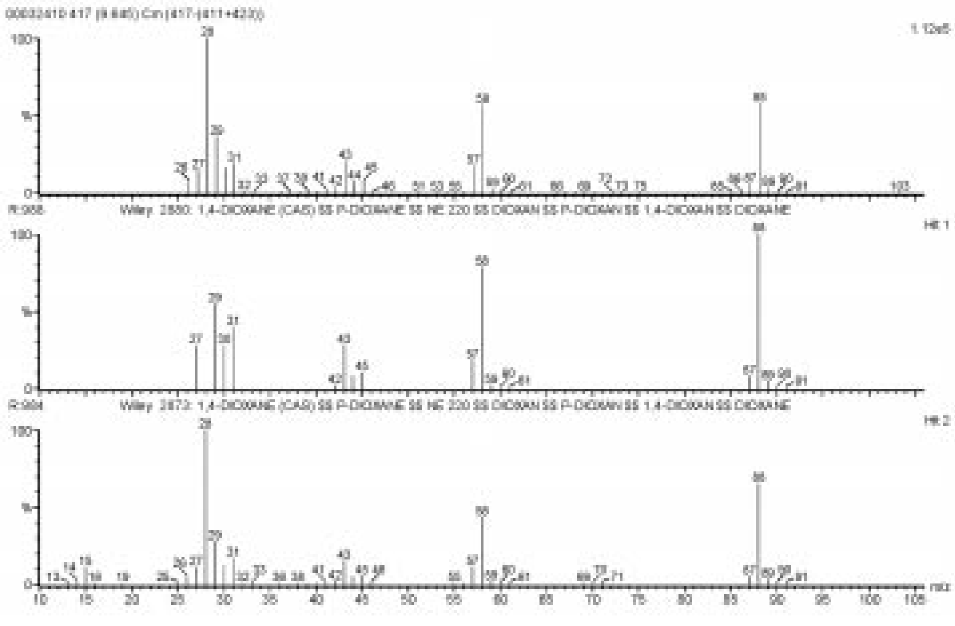

Fig. 2c Mass spectra of one of the major GC peaks, as well as the two best fits from Wiley’s library of mass spectra

tance of regularly running TG blank runs. The variation in retention times on the *n*-octyl acetate for the three chromatograms is within the expected reproducibility for the analysis. The identification could further have been confirmed by analysing a standard solution of *n*-octyl acetate injected on to the sample tube. This was not regarded here as necessary.

Decomposition of a typical production chemical

Production chemicals are added to the oil or gas for specific purposes. Some commonly used types are emulsion breakers, antifoams and corrosion inhibitors. They have in common that once added they go through the same processing as the oil/gas, which always includes changes in temperature. There are examples in the literature which show that for instance antifoams decompose once heated and lead to silicon poisoning of catalysts [9]. It has also been observed that fuel additives which contain polymer-type materials will degrade and change their properties once heated in air [10]. In this context, it was of interest to establish a laboratory method for inducing and studying such changes in chemicals. The example below shows how the TG instrument in combination with TG evolved gas analysis can be used for this purpose.

Triethylene glycol, abbreviated TEG, is an often used production chemical for drying natural gas. There have been repeated concerns that this chemical can decompose and so be lost into the gas phase and create technical problems downstream the processing equipment or alternatively lead to product contamination.The TGA7 was used here to induce thermal decomposition, and evolved gas analysis was carried out using the sample tubes. A typical mass loss curve is shown in Fig. 2a. The chemical evaporates completely below 200°C. The gas chromatogram of the evolved gas is shown in Fig. 2b. It is dominated by a peak at 32.3 min which has been identified as TEG. However, the chromatogram also shows a range of other peaks. Some of the major ones were identified from their mass spectra (see peak annotation in Fig. 2b). One of these spectra is shown in Fig. 2c, where it is compared with the two best matching spectra in Wiley's library, both identifying the compound as 1,4-dioxane. The identification was confirmed by analysing a standard solution of 1,4-dioxane injected on to a sample tube. In the same way 2-methyl-1,3-dioxolane, 1,3-dioxolane, 2-methoxyethanol, 2-ethoxyethanol, nonanal, 1,2-ethanediol diformate and 2-(2-methoxyethoxy)-ethanol were also identified as decomposition products.

Voorhees *et al.* [11] who studied the decomposition of polyethylene glycol found a whole range of products after heating to 450°C. Their experimental set-up was slightly more complex than the one used here, but they also used a similar Tenax adsorbent for the trapping of evolved gas. They detected the 1,4-dioxane, 1,3-dioxolane, 2-methoxyethanol and 2-(2-methoxyethoxy)-ethanol, besides a range of other compounds not identified in this work. Triethylene glycol could be looked upon as a short chain polyethylene glycol, and is therefore likely to give some of the same decomposition products.

Voorhees *et al.* [11] applied cryogenic sampling, and in this way they trapped the more volatile decomposition products too, like carbon dioxide, ethylene oxide and methoxyethane. In our experiments the very volatile compounds would not be adsorbed to the Tenax TA. Instead of using cryogenic sampling another, stronger adsorbent could be used, e.g. Carboxen 1000.

Advantages and disadvantages of the TG evolved gas analysis set-up

The main advantages of this method are the easiness of collecting evolved gas samples while at the same time having the full breadth of GC/MS analysis available. As no major modification of the instrumentation is required to carry out this evolved gas analysis it is ideally suited for upgrading older TG equipment. It provides a less expensive alternative than on-line analysis. As the GC/MS is free-standing and thus not occupied continuously it may also be used for other purposes.

Another advantage is that the sample is more concentrated when adsorbed on the sample tube than if the sample is directly transferred to the GC/MS by the purge gas from the TGA7. Furthermore, because of the availability of the GC, separation of overlapping decomposition products is also achieved.

A limitation of the instrumentation is that the method is strictly qualitative because the amount of evolved gases that is adsorbed in the sample tube is not known. Also, the adsorbent may constitute a limitation as it adsorbs only certain compounds. The latter could be overcome by using other adsorbents. Different adsorbents can be used in combinations in the same sample tube, and in this way compounds in a wide range of volatility could be adsorbed. A minor drawback is that there are several steps where contamination can occur. However, this can be monitored by running blank samples regularly.

Conclusions

It has been shown that off-line TG evolved gas analysis using GC/MS is easily accomplished by collecting the gas in sample tubes filled with the adsorbent Tenax TA. This combination of instrumentation can be used for the identification of unknown components in production chemicals. It can also be used to induce thermal decomposition and thus help to identify possible by-products or contaminants in processed oil and gas.

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We would like to thank Dyno Oil Field Chemicals for permission to use three of their production chemicals as test materials.

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