

Basics of the Quantification of the Spectroscopic Signals Recorded in TA-MS and TA-FTIR Systems



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Generally, the interpretation of thermoanalytical curves does not cause difficulties if the investigated reaction proceeds via one or more well resolved steps and stoichiometry and composition of the reactant, intermediate(s) and product(s) are known. Unfortunately, frequently the temperature ranges of the various decomposition stages, particularly in multicomponent systems, overlap each other and the exact composition of the evolved gaseous products is unknown. The proper interpretation of recorded signals requires coupling of TA with techniques which allow continuous monitoring of the gas composition, such as gas chromatography (GC), Fourier transform infra-red spectroscopy (FTIR), and mass spectrometry (MS).

The main application of the TA-MS and TA-FTIR techniques is the identification of the gaseous products, which together with the thermal effects (DTA) and mass changes (TG), aids in interpreting the course of the investigated reaction. The qualitative MS analysis is routinely done by comparing the recorded spectra with key fragment ions and their relative intensities for known elements and compounds. In complex mixtures the identification of the gases can be better done by infrared spectroscopy. For both techniques the large libraries of MS and IR spectra of gases and vapours are available.

Very important, but difficult problem is the quantitative interpretation of spectrometric data, which needs the calibration of the system, i.e. the determination of the relationship between the observed intensities of the ion currents (MS) or IR-spectra and the amount of the analysed species.

The common method of calibration of spectrometric signals is based on the determination of the relationship between their intensities and concentration of the calibrated gas. However, this method is time consuming and requires the application of gaseous mixtures with well-defined composition. An additional difficulty is that such calibration is usually performed at room temperature, while

during the thermal decomposition the temperature of the gas phase often changes considerably what can render the results obtained by calibration at low temperature doubtful.

Here we report a systematic study of the influence of experimental parameters (carrier gas flow rate, amount of analyzed species, temperature, and kind of carrier gas) on the course of spectroscopic curves measured in combined TA-MS and TA-FTIR systems. The quantification of the signals was done by PulseTA[®] technique [1,2] based on the injection of the known amount of gases or liquids into the carrier gas stream flowing over the investigated samples. The main conclusions are as follows:

(i) The investigated TA-MS and TA-FTIR systems show linearity between the amount of the analyzed species and the corresponding spectrometric signals even when the sample mass is increased by a factor of ten.

(ii) For the capillary coupling the sensitivity of the spectrometric signals do not depend on the temperature in the range 20-1000°C. This important conclusion enables quantitative evaluations of MS- and FTIR curves obtained at any temperature using a single-point calibration. For the Skimmer[®] system the additional calibrations are required.

(iii) The relative intensity of the MS signal (i.e. related to the unit of carrier gas flow rate) is constant in a wide range of flow changes. A decrease of the flow rate is advantageous for the qualitative recognition of very small signals, but leads to a distinct broadening and shifting of the signal to higher temperatures.

(iv) The described methods of calibration facilitate a quantitative interpretation of MS and FTIR signals with an accuracy of a few percent. The lower limit of the detection, depending slightly on the properties of investigated samples and kind of evolved species, lies distinctly below 0.1 wt%. In certain cases the amounts lower than 0.01 wt% were quantified.

The application of the PulseTA[®] for quantifying evolved gases will be illustrated using examples from material science and catalysis.

References

1. M. Maciejewski, C. A. Müller, R. Tschan, W.-D. Emmerich and A. Baiker, *Thermochim. Acta*, 295 (1997) 167.
2. M. Maciejewski and A. Baiker, *Thermochim. Acta*, 295 (1997) 95.