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Quantitative TG-MS analysis of evolved gases during the thermal decomposition of carbon containing solids

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ABSTRACT

Quantitative thermogravimetry-mass spectrometry (TG-MS) method was developed for the determination of the composition of gases evolved during the decomposition of solids. The present method is based on the linear relationship between the amount of evolved gases and the peak area for corresponding fragment ion via proportionality constant (K) which gains the similar values for all evolved gaseous products. Determination and verification of K were performed with the various initial mass of $CaC_2O_4{\cdot}H_2O$ decomposing with the evolution of H_2O, CO, and CO_2. The resulted values of the proportionality constants reach $(3.32 \pm 0.11) \times 10^7$ for H_2O, $(3.35 \pm 0.08) \times 10^7$ for CO, and $(3.27 \pm 0.07) \times 10^7$ for CO_2. The developed TG-MS method was verified at the decomposition of $(COOH)_2{\cdot}2H_2O$, $NaHCO_3$ and HCOONa. By applying the average value of K for the determination of the composition of gaseous products evolved from the previously mentioned three substances, a quite good correspondence between theoretically and experimentally calculated composition can be found. The results imply that developed TG-MS method might be a useful tool to detect quantitatively the amount of evolved gases during the thermal decomposition of carbonaceous materials.

1. Introduction

The combination of thermal analysis and mass spectrometry (TG-MS) allows obtaining especially qualitative information about the composition of evolved gases during the thermal decomposition of solids. The possibility of obtaining quantitative information from TG-MS analysis (composition of gaseous products) is not used very often and up to now only a few authors concerned with it [1–6]. The published methods are based on individual calibration of MS signal (determination of calibration constant) for individually detected gases. Calibration of MS signal can be performed by the heating of different amount of pure substance which thermally decomposes according to known stoichiometric reaction. For this purpose various reference materials can be used e.g. $NaHCO_3$ (H_2O and CO_2) [1–3], $KHCO_3$ (H_2O and CO_2) [4], MgC_2O_4 (CO and CO_2) [1], $CaC_2O_4{\cdot}H_2O$ (H_2O, CO and CO_2) [2] or some pure natural minerals such as $CaSO_4{\cdot}2H_2O$ (H_2O), $CaCO_3$ (CO_2) or Fe_2O_3 (O_2) [5].

Several criteria should be met by the TG-MS system to obtain reproducible results. The high flow stability through the TG-MS system and constant pressure in the MS system are certainly required. Both commonly used systems interconnecting TG and MS (capillary or direct input) should ensure this requirement, but the interconnection is always dependent on intensity of use (e.g. number of measurements, character of evolved gaseous product etc.). Furthermore, the intensity of the MS signal should not be affected by the temperature in the TG furnace. Only, in this case, the calibration curve obtained from the decomposition of solids at the specific temperature will be valid for the quantitative determination of evolved gases at another temperature. Finally, the intensity of the MS signal should not be affected by the heating rate applied in the TG analysis to ensure that the TG-MS analysis is carried out under chemically controlled conditions [4].

Accomplishing all these system requirements together with complicated and time-consuming calibration for different gases is probably a reason for the infrequent use of TG-MS measurements for quantitative analysis of evolved gases.

Thus, the aim of this work is development and testing of the simplified quantitative TG-MS approach enabling direct determination of the composition of evolved gases. The presented quantitative TG-MS method is based on two assumptions. The first assumes that the amount of evolved gases during the thermal decomposition of the sample is proportional to the peak areas of fragment ions via some constant of proportionality (K) (this assumption is common in all published methods [1–5]). The second supposes that the value of the proportionality constant will be the same for

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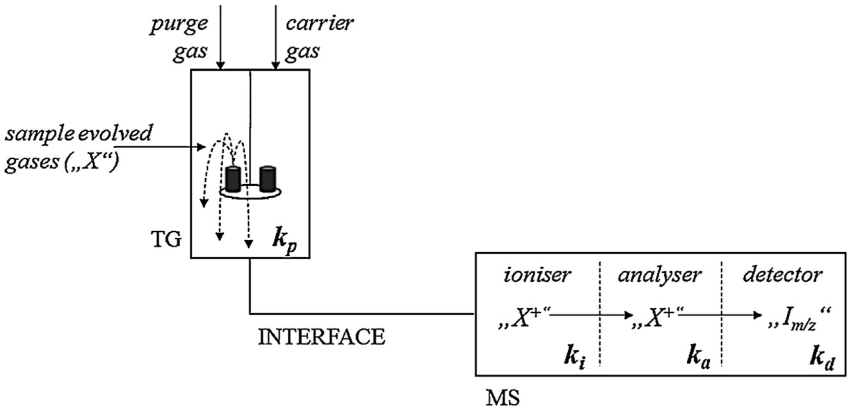

Fig. 1. Model of TG-MS measuring system with the distribution of individual constants (k_x).

all evolved gases. This hypothesis is to be proved in the present work.

2. Theory

Detection of evolved gases during TG experiment by MS system involves several steps (Fig. 1). Only small part of n_x evolved molecules of gas X (given by transfer constant k_P) is transferred into ion source and ionised. The most of gaseous compounds gives various ions during ionisation, so only part of molecules is ionised to specific ion X^+ (ionisation constant k_i). The ionised ions are then transferred through the analyser (k_a) into the detector (k_d).

Based on these expectations, the experimentally obtained area of the peak on MS signal ($A_{m/z}$) for ion X^+ measured during thermoanalytical experiment is proportional to the amount of gaseous products (n_x) evolved from the sample in the furnace (Eq. (1)).

$$A_{m/z} = n_x \times k_p \times k_i \times k_a \times k_d \tag{1}$$

It can be assumed, that constants (k_a, k_d) depend only on a construction of MS and remain constant for different gases during the different experiments. Constant (k_p) is also equal for different substances, but it can be changed between experiments due to clogging of the TG-MS interface. On the other hand, constant (k_i) is different for various ions, but it can be obtained from the mass spectra database (e.g. NIST MS Search v.2.0 [7]). Based on mentioned information it is possible to express the individual constants (k_p, k_a, k_d) as one constant K (constant of proportionality) which is independent of the type of ions. Thus, the Eq. (1) can be rearranged as follows:

$$n_x = \frac{1}{k_p \times k_a \times k_d} \times \frac{A_{m/z}}{k_i} = K \times \frac{A_{m/z}}{k_i} \tag{2}$$

The Eq. (2) is valid for peaks of MS signals corresponding to simple ion. For example, in the case of H_2O the relationship between the amount of evolved gas and the peak area can be expressed very simply because the signal with the highest intensity is caused only by one substance (in the most decomposition experiments). The values mentioned in Table 1 (obtained from the MS spectra database) imply that 81.35% molecules of water are ionised to the ion with $m/z = 18$; 17.26% to the ion with $m/z = 17$ etc. Thus, the equation for H_2O molecules can be expressed as follows in Eq. (3):

$$\begin{aligned} n_{H_2O} &= K \times (A_{18} + A_{17} + A_{16} + A_{19} + A_{20}) \\ &= K \times \frac{A_{18}}{0.8135} = K \times \frac{A_{17}}{0,1726} = \ldots \end{aligned} \tag{3}$$

In the opposite case (e.g. signal $m/z = 28$ can be composed from contributions of CO but also CO_2, if present) the Eq. (2) becomes more complicated.

However, if the evolution of a certain amount of gaseous products ($X_1 \ldots X_n$) during the decomposition causes the mass loss (Δm), following Eq. (4) is valid.

$$\Delta m = \sum \left(n_{X_i} \times m_{X_i} \right) \tag{4}$$

The solution of the mentioned general Eqs. (2) and (4) leads to values of the proportionality constant (K) and the molar amounts of released gaseous products (n_x). The form of the equations for the concrete gaseous products evolved during the thermal decomposition of the studied substances will be demonstrated bellow in Section 4.

3. Experimental

Thermoanalytical experiments (TG-MS) were performed using SetsysEvolution (Setaram) with a quadrupole mass spectrometer QMG 700 (Pfeifer) directly coupled by a SuperSonic system (Setaram). In the SuperSonic system, the evolved gases are accelerated by a two steps pressure drop system. Their speed is overcoming the speed of sound and they are instantaneously transferred through the sampling orifice (primary vacuum, 10 Pa) and skimming cone orifice (secondary vacuum, 10^{-3} Pa) to the ion source (crossbeam, tungsten filament, cathode voltage −70 kV, emission current 1.0 A), avoiding any condensation or recombination of the molecules [8]. Detection of the fragment ions is conducted by Faraday detector. The measurements for determination and verification of proportionality constant were performed with different amounts of the standard compound ($CaC_2O_4 \cdot H_2O$, Sigma-Aldrich) ranging from 1 to 20 mg (9 measurements) in crucible from α-Al_2O_3. TG-MS curves were recorded under an argon atmosphere (flow rate 20 ml min^{-1}) from 15 °C to 1000 °C with heating rate 10 K min^{-1}. The MS signals corresponding to H_2O ($m/z = 18$), CO ($m/z = 28$), O_2 ($m/z = 32$) and CO_2 ($m/z = 44$) were monitored in MID mode (multiple ion detection).

Developed quantitative TG-MS method was verified at the compounds with the known thermal decomposition, concretely $(COOH)_2 \cdot 2H_2O$ (p.a., MACH chemikálie), $NaHCO_3$ (p.a., Penta) and HCOONa (p.a., LACHEMA). The measurements of these three compounds were carried out with the use of 5, 10 and 15 mg of sample under the condition identical to that for the thermal decomposition of $CaC_2O_4 \cdot H_2O$. The monitored MS signals were selected according to the expected thermal decomposition of the individual compounds.