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A method for the quantitative analysis of gaseous mixtures by online mass spectrometry

Zaizhe Cheng [a,b], Tibra Mozammel [a,c], Jim Patel [a], Woo Jin Lee [a], Shouying Huang [b], Seng Lim [a], Xinbin Ma [b], Suresh Bhargava [c], Chao'en Li [a,*]

[a] CSIRO Energy, 71 Normanby Road, Clayton North, Victoria, 3169, Australia
[b] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[c] School of Sciences, RMIT University, 124 La Trobe Street, Melbourne, Victoria, 3000, Australia

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ABSTRACT

Online mass spectrometry is a widely used technique in tracking composition changes of gas mixture during the reaction. This paper reports a quantification analysis method of gas mixtures detected by an online mass spectrometry. In this analysis, a mass spectrum correction coefficient matrix is generated based on the calibration of mass spectrometry intensities of premixed calibration gas mixtures, and then the concentrations of gas components are calculated from this matrix by subtracting the interferences of other components with overlapped peaks. The accuracy of obtained results were verified by online gas chromatography in the meanwhile. The detailed error analysis was supplied in a separate supplement document. This method can be applied on the online detection of gas phase reactions with promising advantages to analysis of online gas chromatography, which is suitable for analysis of spectra overlaps (a given *m/z* signal contributed from two or multiple components) and kinetic studies.

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1. Introduction

Mass spectrometry is an important tool for analyzing trace gas compositions, molecular weights, and structure of unknown substances [1], by measuring the specific mass-to-charge ratios (*m/z*) of ion fragments broken down from gas component molecules. One of general applications of mass spectrometry is for the online reaction monitoring, the benefits of which are from rapid analytical method and real-time feedback of the reactor. The most widely used quadrupole mass spectrometer [2] consists of four parallel cylindrical electrodes rods responsible for filtering sample ions, based on their mass-to-charge ratios [3].

Traditionally the gas chromatography (GC) analysis method is widely employed for the quantification of online gas mixtures [4,5]. The equipped quantitative loop with thermal conductivity detector (TCD) and flame ionization detector (FID) have provided a relative accurate quantification way to calculate the component concentrations. However, the online GC analysis also suffers from several fundamental restrictions. For example, it requires a time-wasting pre-separation procedure, during this period the oven is heated to separate the chemical compounds in the chromatographic column. Thus it will encounter difficulties when dealing with thermodynamically unstable compounds, and the essential time-consuming pre-separation procedures make the GC analysis discontinuous during the online gas flow, which limit its application on short-time reactions. In addition, the identifiability of compounds relies on the type of separation columns. Some compounds are only analyzed by proper columns.

Notably, the mass spectrometry analysis is a potential method for the continuous detection of online gas mixtures. As its sensitivity is usually several orders of magnitude higher than GC analysis, [6,7] the mass spectrometry can be employed for the analysis of trace gas molecules. Moreover, the range of the molecules available for mass spectrometry detection is much wider, including some small weight and unstable or sticky molecules that cannot be practically analyzed by GC [8,9]. Thus the mass spectrometry analysis has been widely carried out for the gas phase reactions, such as cyclic redox water splitting process [10] and chemical-looping combustion process [11].

As the mass spectrometry signals are seriously affected by the operating conditions, [12,13] it is not easy to quantify gas mixtures only depending on mass spectrometry, the online quantification methods in regard to mass spectrometry are mainly about GC–MS [14], selected ion flow tube mass spectrometry (SIFT-MS) [1,15] and

Nomenclature

a	A constant
f_{ij}	Integrated calibration factor
F_j	The calibration coefficient factor of the main fragment of compound j
I_{ij}	Ion current contributed by j^{th} gaseous compound at i^{th} m/z
I	The vector of ion currents
$I_{R,ij}$	The relative intensity of ith fragment to the main fragment for compound j
I_e	The electron emission current
P_j	Partial pressure
P	The vector of partial pressures
P_{MS}	The operating pressure of the mass spectrometer
T_{ij}	The transmission of the fragment at i^{th} m/z
σ_{ij}	The ionization cross section
λ_e	The mean free path of the electrons
η_{ij}	The gain of the secondary electron multiplier
Φ	The square calibration coefficient matrix

other combined instruments [16]. Vylegzhanin et al.[17] proposed a procedure to calculate concentrations of components in a mixture by solving a pseudoinverse matrix from the assumption that Bouguer's law holds for each component and the principle of additivity holds for the mixture as a whole. Kaiser et al. [18] presented a approach to quantify complex gas mixtures, combining quadrupole mass spectrometry and matrix interval algebra, but the calibration factors are not universal because the calibration strongly depends on the operating conditions of each quadrupole mass spectrometer. Cook et al.[19,20] introduced a quantitation approach using least-squares analysis. This method also requires acquisition and storage of reference spectra of pure components. Mixture spectra are considered as linear combinations of those reference spectra. This method was applied in ethylene oxide production, ten components were determined simultaneously by using process mass spectrometry [19]. However, because it is difficult to precisely duplicate the mass spectrometer parameters in each run, nearly all quantification methods were used to determine the relative concentrations rather than attempting to determine the absolute concentrations from absolute signal intensities.

In this paper, based on Kaiser's work, a rigorous online quadrupole mass spectrometry quantification method of gas mixtures has been developed, this method took advantage of the relative ion current intensity of different fragments to the main fragment from one parent molecule, especially suited for the quantification of complex gas mixtures with mass overlaps. Moreover, careful calibrations and error analysis for included compounds were carried out (See supplement 2), experiments with two different reaction sets were performed as quantification examples, and the results were verified by a paralleled GC analysis.

2. Experiments

2.1. Configuration of on-line mass spectrometry

The apparatus for on-line mass spectrometry analysis was designed as presented in Fig. 1. Here we describe the configuration using two test experiments: methane dry reforming, and direct synthesis of hydrogen peroxide (H_2O_2) from hydrogen and oxygen. The outlet gas mixtures of these two reactions consist of H_2, He, CH_4, H_2O, C_2H_2, N_2, CO, C_2H_4, C_2H_6, CH_3OH, O_2, Ar, CO_2 etc. The MS signals of fragments of these molecules are various and typical for this mass spectrometry method. G-01 is the flammable gas cylinder,

methane (99.94%, BOC, Australia) or 4% hydrogen in argon (4.04%, BOC, Australia), G-02 is the oxidizing gas cylinder, CO_2 (99.99%, BOC, Australia) or 5% oxygen in argon (4.96%, BOC, Australia), and G-03 is the inert gas cylinder, argon (99.999%, BOC, Australia). All the three gases are metered to the reactor with respective Brooks mass flow controllers (MFCs). The outlet gases of the reactor are online detected by a quadrupole mass spectrometer (OmniStar Pfeiffer, Scitek, Australia) and a gas chromatographer (SHIMADZU GC-2014, Australia) simultaneously. The mass spectrometer covers the m/z range of 1–300, and is equipped with a capillary which can be heated up to 350 °C to prevent vapors from condensing during the analysis. During the experiments, the MS signals of all fragments of H_2, He, CH_4, H_2O, C_2H_2, N_2, CO, C_2H_4, C_2H_6, CH_3OH, O_2, Ar, CO_2 etc. were recorded continuously depending on the reactions carried out. Prior to the calculation of component concentrations, a careful calibration for each component was carried out to get the calibration coefficient. The GC is equipped with a methaniser and a flame ionization detector (FID) for the analysis of gas phase carbon related components such as CH_4, CO, CO_2, C_2H_2, C_2H_4, and C_2H_6, and a thermal conductivity detector (TCD) for the analysis of non-carbon components such as H_2, He, N_2, and O_2.

2.2. Calibration

As the calibration coefficients vary with many factors and the ion currents are afflicted by the current instrument operating conditions of the mass spectrometer, which will be discussed in details in Section 3, it is necessary to conduct the calibration experiment. In this article, the calibrations of all components were conducted carefully at different concentrations, respectively. In order to make the quantification more accurate and feasible, the chosen calibration concentrations are close to the actual concentrations in the reaction. The gas flow rate was accurately controlled by MFCs. From the mass spectrometry intensity signals and the corresponding concentrations, a linear calibration curve can be obtained and then a correlation parameter set of a slope and an intercept between the gas component concentration and mass spectrometry intensity signal is calculated. The calibrations for liquid components (i.e. H_2O and methanol) were carried out by bubbling the liquids with argon. As the concentrations of argon corresponding to different intensities have been obtained from the argon calibration curve with different gas mixtures, the vapor concentrations of liquid components in argon are the residual. The mass spectrometry intensities of liquid components in argon at different concentrations were obtained by heating the liquids at different temperatures when bubbling due to the vaporization increases with the rise of temperature.

3. Quantification method

3.1. Calculation theory

Normally the ion current (I_{ij}) contributed by j^{th} gaseous compound at i^{th} m/z in a mass spectrometer has the following linear relationship to the partial pressure P_j:[18]

$$I_{ij} = P_j I_e \lambda_e \eta_{ij} T_{ij} \sigma_{ij} a = f_{ij} P_j \tag{1}$$

where I_e is the electron emission current in the mass spectrometer, λ_e is the mean free path of the electrons, η_{ij} is the gain of the secondary electron multiplier, T_{ij} is the transmission of the fragment at i^{th} m/z, σ_{ij} is the ionization cross section, a is a constant, and f_{ij} is an integrated calibration factor of all these above parameters. The value of constant f_{ij} can be calculated by measuring the mass spectrometer signal of gas j at its ith m/z and pressure P_j. As the mass spectrometer is not equipped with separation unit, when