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Analyte quantification with comprehensive two-dimensional gas chromatography: Assessment of methods for baseline correction, peak delineation, and matrix effect elimination for real samples

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ABSTRACT

Comprehensive two-dimensional gas chromatography (GC × GC) is used widely to separate and measure organic chemicals in complex mixtures. However, approaches to quantify analytes in real, complex samples have not been critically assessed. We quantified 7 PAHs in a certified diesel fuel using GC × GC coupled to flame ionization detector (FID), and we quantified 11 target chlorinated hydrocarbons in a lake water extract using GC × GC with electron capture detector (μECD), further confirmed qualitatively by GC × GC with electron capture negative chemical ionization time-of-flight mass spectrometer (ENCI-TOFMS). Target analyte peak volumes were determined using several existing baseline correction algorithms and peak delineation algorithms. Analyte quantifications were conducted using external standards and also using standard additions, enabling us to diagnose matrix effects. We then applied several chemometric tests to these data. We find that the choice of baseline correction algorithm and peak delineation algorithm strongly influence the reproducibility of analyte signal, error of the calibration offset, proportionality of integrated signal response, and accuracy of quantifications. Additionally, the choice of baseline correction and the peak delineation algorithm are essential for correctly discriminating analyte signal from unresolved complex mixture signal, and this is the chief consideration for controlling matrix effects during quantification. The diagnostic approaches presented here provide guidance for analyte quantification using GC × GC.

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1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is used widely for the analysis of complex mixtures, as it can resolve thousands of peaks within single chromatograms [1,2]. GC × GC has been used in the analysis of petroleum, environmental samples, foods, and biological fluids [1]. Even though GC × GC provides very good separation capacity, analyte co-elution still arises in very complex samples [3]. Analyte quantification remains challenging due to the inherent complexity of two-dimensional data and the typical presence of co-eluting (overlapping) peaks [4,5].

During the past decade, several investigations have quantified analytes using GC × GC data [5]. In 1998, Beens et al. introduced the notion of analyte quantification with GC × GC-FID, employing the external standard calibration method [6]. Later studies applied external standard calibration as a means to quantify small aromatic hydrocarbons in gasoline, suspected allergens in fragrances, and polychlorinated biphenyls (PCBs) in soil and sediment [2,7–10]. Some of these studies used internal standards to normalize the peak volumes of the target analytes [2,7,10]. The studies mentioned above used univariate detectors, either FID (flame ionization detector) or ECD (electron capture detector). These were important contributions to the development of quantification methods for GC × GC. However the analytes quantified in these studies were usually well-resolved peaks at high concentrations [2,8–10]. Kallio and Hyötyläinen emphasized the necessity of well-resolved peaks in order to achieve accurate integrated peak volumes [9]. Additionally, Adahchour et al. expressed concern regarding the quality of quantifications performed on univariate data produced by GC × GC

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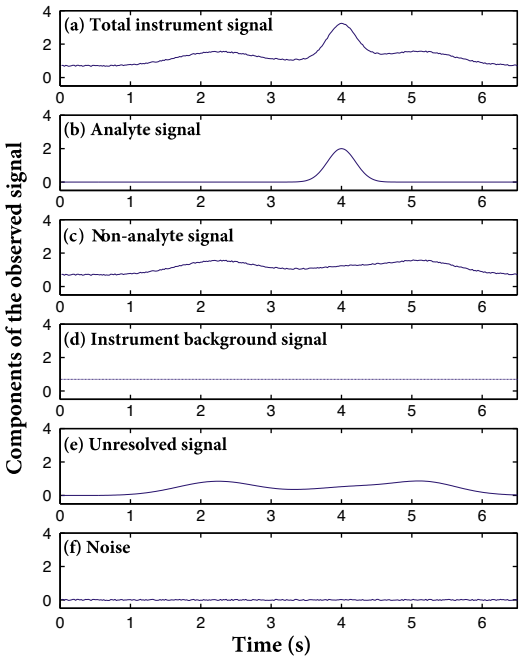

Fig. 1. Conceptual schematic of the disaggregated components of the sample signal in a single modulation period of the GC × GC chromatogram. (a) The observed total instrument signal; (b) the resolvable analyte signal; (c) the non-analyte signal; (d) the instrument background signal; (e) the unresolved signal; and (f) the noise.

using the external standard calibration method [11]. They stated that external calibration was not suitable for quantification in cases involving poorly resolved peaks.

The complexity of typical GC × GC chromatograms warrants sophisticated data processing methods [4,5,12,13]. After data acquisition, analyte signal quantification involves the following major data processing tasks: baseline correction, peak detection, and peak delineation [12–16]. To facilitate discussion of these different data processing operations, we conceptually decompose the GC × GC detector signal into four additive components (Fig. 1; Eq. (1)), defined as follows:

- The *resolvable analyte signal* is the signal attributed to analytes that are wholly or partly resolved by the instrument [12,13,17]. We do not assign a threshold of chromatographic resolution [18] to the resolvable analyte signal, since the ability to differentiate resolved signal from unresolved signal depends upon the baseline correction and peak delineation algorithms applied. In the present work, we are interested in quantifying resolvable analyte signal, or peak volume, of target analytes.
- The *unresolved signal* arises from chemical elutants that are not reasonably resolved from one another. This is operationally defined by the combination of baseline correction and peak delineation algorithm applied. The unresolved signal corresponds to the "chemical blank" in earlier chemometrics literature [19,20]. The *matrix effect* arises from failure to discriminate properly between the unresolved signal and the resolvable analyte signal. Matrix effects are defined and explained further in Section 2.6.
- The *instrument background signal* is the signal produced by the instrument in the absence of sample, excluding random signal fluctuations.
- The *noise* is zero-mean random fluctuation of the signal, inherent to the instrument detector [4,12].

Distinguishing and separating these signal components is an important goal of GC × GC data processing. Since here we are focused on analyte quantification, we also define the *non-analyte signal*, which is the unresolved signal plus instrument background signal plus noise (Eq. (1)). The non-analyte signal is called the "constant error" in earlier chemometrics literature [21], and this signal component can be quantified by measuring the Total Youden Blank, assuming that non-additive signal interactions (matrix interferences) are not present [19,22].

$$\begin{aligned}\text{Total instrument signal} = {} & \text{analyte signal} \\ & \left.\begin{aligned}&+\text{instrument background signal}\\ &+\text{unresolved signal}\\ &+\text{noise}\end{aligned}\right\}\ \text{non-analyte signal}\end{aligned} \tag{1}$$

Throughout this article, we refer to a *peak integration method* as a particular combination of algorithms that leads to a unique value for the integrated resolvable analyte signal, or peak volume, attributed to a given analyte in the GC × GC chromatogram. An individual peak integration method is composed of one baseline correction algorithm combined with one peak delineation algorithm. These methods are discussed below. The term *quantification method* refers to a method that uniquely maps an observed peak volume to an estimated analyte concentration in an environmental sample. For this purpose, we applied both the external standard calibration method (ESM) and the standard addition calibration method (SAM) [23–25], explained in Section 2.6.

After signal acquisition, the first step in GC × GC data processing is usually the baseline correction, which involves estimation and removal of the baseline. Here, the baseline is defined operationally as the signal that is subtracted from the total chromatogram signal before peak integration [4,12]. The approach taken for defining the baseline may vary depending on the objective of the analyst. For example, for quantification of resolvable analytes, an appropriate baseline correction method ideally should remove the non-analyte signal component, leaving behind only the resolvable analyte signal [12,13,26,27]. Alternatively, for the quantification of the sample total chemical signal, it may instead be desirable for the baseline correction method to remove only the instrument background signal component, leaving behind both the resolvable analyte signal and the unresolved signal [26,27].

Several strategies have been proposed for performing a baseline correction [4]. It may be appropriate to define the analytical blank as the baseline and remove this signal from the sample signal. The analytical blank is defined as a sample identical to the original sample, but excluding the analyte of interest [25]. In principle this should produce the non-analyte signal chromatogram. However it is often not possible to obtain the analytical blank [12]. Available automated algorithms offer more general approaches to estimating the baseline. The "deadband baseline" correction algorithm uses the statistical properties of white noise to define regions of the chromatogram called deadbands and then calculates and removes this signal from the chromatogram [16,28]. The deadband baseline is intended to estimate the signal trend that would arise in the absence of chemical elutants [16]. This baseline correction algorithm thus estimates and removes the instrument background signal, but it does not remove the unresolved signal component (Fig. 1). A second algorithm, the "local linear baseline" correction, fits a straight line to intervals as wide as the peak width within each modulation period of the GC × GC chromatogram, which is then subtracted from the total instrument signal [4]. The local linear baseline correction method thus attempts to estimate and remove the non-analyte signal (instrument background signal plus unresolved signal and noise), leaving behind the resolvable analyte signal. However, complications can arise in cases of the presence of unresolved material and low signal-to-noise ratios [12]. Finally, the Eilers algorithm takes a different approach, which is to

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