



# Comparison of gas chromatography-combustion-mass spectrometry and gas chromatography-flame ionization detector for the determination of fatty acid methyl esters in biodiesel without specific standards



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## ABSTRACT

GC-FID has been effectively used as a universal quantification technique for volatile organic compounds for a long time. In most cases, the use of the ECN allows for quantification by GC-FID without external calibration using only the response of a single internal standard. In this paper we compare the performance characteristics of GC-FID with those of post-column  $^{13}\text{C}$  Isotope Dilution GC-Combustion-MS for the absolute quantification of organic compounds without the need for individual standards. For this comparison we have selected the quantification of FAMES in biodiesel. The selection of the right internal standard was critical for GC-FID even when ECN were considered. On the other hand, the nature of the internal standard was not relevant when GC-Combustion-MS was employed. The proposed method was validated with the analysis of the certified reference material SRM 2772 and comparative data was obtained on real biodiesel samples. The analysis of the SRM 2772 biodiesel provided recoveries in the range 100.6–103.5% and 96.4–103.6% for GC-combustion-MS and GC-FID, respectively. The detection limit for GC-combustion-MS was found to be 4.2 ng compound/g of injected sample. In conclusion, the quantitative performance of GC-Combustion-MS compared satisfactorily with that of GC-FID constituting a viable alternative for the quantification of organic compounds without the need for individual standards.

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## 1. Introduction

The Flame Ionization Detector (FID) can be considered as the most universal and generally used detection method in Gas Chromatography (GC). Organic compounds eluting from the column are burned in a small hydrogen/air flame and, through a set of complex reactions, nearly all carbon atoms are converted into methane which is further oxidised to carbon dioxide. During this process, a small fraction of carbon atoms are transformed into  $\text{CHO}^+$  which generates a small electric current between two electrodes. The FID will detect virtually all carbon containing compounds, with the exception of a limited number of small molecules such as car-

bon monoxide, carbon dioxide, carbon disulfide, formaldehyde and formic acid. In fact, due to its diverse and comprehensive response, it is considered a universal detector for organic compounds in GC. Additionally, FID response has been shown to be linear over nearly seven orders of magnitude with low noise levels, high sensitivity and exceptional reliability [1].

Quantification in GC-FID can be performed in different ways. The external calibration method relies on the comparison of the analyte peak area with the peak area of a series of standards of the compound of interest at different and known concentration levels. In most cases an internal standard is employed to correct for errors during sample preparation and/or injection in the GC. Alternatively, and due to the uniform response of the FID for different organic compounds, other procedures which do not require a calibration graph have been proposed. The so-called “area percent method” is employed traditionally in the petrochemical industry with or without the use of internal standards but this method works better when

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all compounds of interest have the same functional groups. When compounds with different functional groups are analysed, the use of response factors in combination with the Effective Carbon Number (ECN) concept [1] has been proposed for quantification. This later procedure is an improvement on the area percent method as it takes into account the different response in the FID for different organic functional groups. Research on the use of response factors based on the ECN for absolute quantification by GC-FID started more than 50 years ago [1] trying to fulfil the dream of every chromatographer: the development of a universal, absolute and quantitative chromatographic detector which does not require external calibration. Modern books on Gas Chromatography recognize the FID as the detector which has come closer to fulfil this dream [1].

ECN in combination with FID was used for the determination of biogenic volatile organic compounds (BVOCs) emitted into the atmosphere by plants [2]. A dynamic dilution system allowed obtaining quantitative gas standards of VOCs with mixing ratios below 50 ppb. Measured ECN values were within 10% of theoretical ECN values for most terpenoid compounds. Szulejko et al. employed ECN to estimate the response factor values for volatile organic compounds amenable to a sorbent-tube thermal desorption GC-MS method [3]. As well, the ECN approach was positively used on the quantitative analysis of compounds lacking authentic standards or surrogates (CLASS) in environmental media [4]. The same authors also evaluate and improve the ECN-based quantitation procedure of CLASS by using additional descriptors (i.e., -Cl, -Br, >C=C<, and a group ECN offset ( $O_k$ )) using the 1-point RF values [5].

Recently, a procedure for the use of GC-Combustion-MS in combination with post-column carbon isotope dilution has been developed in our laboratory based on a standard quadrupole GC-MS instrument [6]. The combustion reaction secures quantitative conversion of every organic compound eluting from the GC column into  $\text{CO}_2$  providing the required isotopic equilibrium between such compounds and the isotopically-enriched carbon tracer ( $^{13}\text{CO}_2$ ) continuously added. Electron ionization (EI) has been selected, so that ionization could be carried out under a high vacuum to enable much higher sensitivity and lower carbon contamination. Finally, the isotope ratio (44/45) in the mixture is measured as a function of time by means of MS.

Later, a commercial GC-IRMS instrument has been modified to allow the continuous introduction of a post-column flow of  $^{13}\text{CO}_2$  through a splitter holder located inside the chromatographic oven [7]. As the instrumental modification occurs after the chromatographic separation and before the entrance to the combustion reactor, the isotopic equilibrium between the natural  $\text{CO}_2$  from the sample and the  $^{13}\text{CO}_2$  used as isotopic tracer is reached in the combustion oven and before the entrance to the ion source. In theory, this procedure should provide quantitative information of every single compound previously separated in the chromatographic column without the need for individual standards or response factors, providing a generic and universal detector.

The feasibility of the post-column Isotope Dilution procedure in combination with GC-Combustion-MS has been successfully evaluated first, for organic compounds corresponding to different families ( $\text{C}_9$ – $\text{C}_{20}$  n-alkanes, BTEX and esters) [8] and, later, to high boiling point compounds (PAH) and heteroatom-containing compounds (polychlorinated biphenyls (PCBs) and benzothiophens) [7].

So, the objective of this study was to evaluate the post-column  $^{13}\text{C}$  Isotope Dilution GC-Combustion-IRMS procedure and compare it with alternative methods based on GC-FID. For this purpose we have selected the determination of Fatty Acid Methyl Esters (FAMES) in biodiesel because standard method EN-14103 specifies

GC-FID as the instrument to be employed and the quantification is based only on the response of a single internal standard.

Biodiesel is a clean-burning alternative fuel derived from vegetable oils, animal fats or microbial oils. It is obtained by reaction of the oil- or fat-containing triglycerides with an alcohol, mostly methanol, in the presence of a catalyst. As a result, the two main reaction products are a mixture of FAMES and glycerol, considered as a high value co-product [9]. Biodiesel must fulfil accepted standards before usage. In the United States, specifications are set by the American Society for Testing and Materials (ASTM) through standard ASTM D6751 [10]. At European level, the quality criteria for the production of biodiesel are specified in standard EN-14214 described by the European Committee for Standardisation (CEN) [11]. The characterization of biodiesel is mandatory in terms of physico-chemical properties but also for origin determination. For both mentioned purposes, the determination of the FAMES profile content is a key parameter [12]. Within the European EN-14214 standard, method EN-14103 specifies the FAMES and linolenic acid methyl ester content in biodiesel [13]. As indicated before, EN-14103 requires GC equipped with FID for FAMES determination and calculation of FAMES content is achieved with the response of a single internal standard. FAMES content is expressed as a mass fraction in percent, and the total FAME content should be greater than 96.5%.

In Norm EN-14103:2003 the range of FAMES is set from C14:0 (methyl myristate) to C24:1 (methyl nervonate) using methyl heptadecanoate (C17:0) as internal standard. Version EN-14103:2011 extends the range from C6:0 to C24:1 and employs methyl nonadecanoate (C19:0) as internal standard to be able to analyse FAMES of animal origin since animal fat can contain higher C17:0 levels [14]. However, it is worth mentioning that the compositional profiles of common vegetable-based biodiesel are mainly dominated by five FAME species: methyl palmitate (C16:0), methyl stearate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2), and methyl linolenate (C18:3) and both internal standards can be employed safely for the analysis of vegetable-based biodiesel.

Although EN-14103 establishes total FAME content determination, in many cases detailed information about the individual FAME content and their distribution could offer an important aspect of production and blending process as well as on the quality control of distribution operations. Recently, Pauls reviewed the most widely used chromatographic techniques for the analysis of biodiesel components. The use of gas chromatography-mass spectrometry (GC-MS), liquid chromatography (LC), or supercritical fluid chromatography has also been reported in the literature for FAMES characterization [15]. Easy ambient sonic-spray ionization mass spectrometry (EASI-MS) [16] has also been evaluated for FAMES characterization. Unfortunately, all these mass spectrometry-based techniques require for specific standards. Recently, infrared spectroscopy (IR) [17] and energy dispersive X-ray fluorescence spectrometer (EDXRF) [18] have been proposed for the determination of global FAMES content in fuel blends (biodiesel + diesel). These techniques provide alternative solution to the determination of unsaturated FAMES which could later be used on the determination of the iodine factor.

So, this study evaluates the post-column  $^{13}\text{C}$  Isotope Dilution GC-Combustion-IRMS method in comparison with EN-14103 method based on GC-FID for total FAMES determination in biodiesel samples. Additionally, the ECN concept [1] has been employed for the determination of individual FAMES by GC-FID and the results compared with GC-Combustion-IRMS. Emphasis was put on the evaluation and selection of appropriate internal standards for both techniques. To demonstrate the suitability of the proposed method, results obtained after analysing the certified reference material SRM 2772 and real biodiesel samples are presented.

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