



Evaluation of a novel helium ionization detector within the context of (low-)flow modulation comprehensive two-dimensional gas chromatography



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ABSTRACT

The present research is focused on the use and evaluation of a novel helium ionization detector, defined as barrier discharge ionization detector (BID), within the context of (low-)flow modulation comprehensive two-dimensional gas chromatography (FM GC × GC). The performance of the BID device was compared to that of a flame ionization detector (FID), under similar FM GC × GC conditions.

Following development and optimization of the FM GC × GC method, the BID was subjected to fine tuning in relation to acquisition frequency and discharge flow. Moreover, the BID performance was measured and compared to that of the FID, in terms of extra-column band broadening, sensitivity and dynamic range. The comparative study was carried out by using standard compounds belonging to different chemical classes, along with a sample of diesel fuel. Advantages and disadvantages of the BID system, also within the context of FM GC × GC, are critically discussed. In general, the BID system was characterized by a more limited dynamic range and increased sensitivity, compared to the FID. Additionally, BID and FID contribution to band broadening was found to be similar under the operational conditions applied.

Particular attention was devoted to the behaviour of the FM GC × GC-BID system toward saturated and aromatic hydrocarbons, for a possible future use in the field of mineral-oil food contamination research.

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1. Introduction

In comprehensive 2D GC (GC × GC), a transfer system, either a cryogenic or flow modulator, is necessary to sample, and inject chromatographic heart-cuts, from the first to the second dimension in a continuous and sequential manner. Analyte bands eluting from the second column are usually narrow both in space and in time. The widths of GC × GC peaks are related to a series of operational parameters, such as modulation conditions, gas linear velocity, stationary phase chemistry, column dimensions, etc. However, and in practically all instances, detectors used in the GC × GC field should be characterized by low dead volumes and a

fast acquisition frequency, to limit extra-column band broadening and for reliable quantification, respectively. Together with mass spectrometry, the most popular detection system used in GC × GC has been the flame ionization detector (FID) [1,2].

FIDs are characterized by a near universal response to organic compounds, good sensitivity, a low dead volume, a fast acquisition frequency (e.g., 250 Hz) and a wide dynamic range. The detector can be considered as a carbon-selective one, with a near equal mass response of C in hydrocarbons. Such a feature enables: (I) the use of a single compound for calibration purposes; (II) the calculation of mass percent composition by considering analyte response relative to the sum of the FID responses for all observed peaks [3].

The discharge helium ionization detector (DHID) is a universal and sensitive detector, which can be used for the analysis of compounds with a poor or no response to the FID, and present in too low amounts for detection with a thermal conductivity detector. Compounds eluting from the capillary column are ionized in a secondary ionization region by high-energy photons generated in a

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Table 1

FM GC × GC-BID/FID conditions of: temperature (Temp.), injector (Inject.) and auxiliary (Aux.) pressures (Gauge), first and second dimension (D1 and D2) gas flows and average linear velocities, loop average linear velocity during accumulation (ALV_{acc}) and re-injection (ALV_{inj}).

Parameter	GC × GC-BID			GC × GC-FID		
	120 °C (standards)	200 °C (FAMES)	40–310 °C (8 °C/min)	120 °C (standards)	200 °C (FAMES)	40–310 °C (8 °C/min)
Temp.						
Initial inject. (kPa)	156.8	192.3	123.7	144.1	180.4	108.6
Final inject.	–	–	187.1	–	–	175.2
Initial aux. (kPa)	73.4	89.7	58.3	54.3	70.8	43.2
Final aux.	–	–	113.7	–	–	101.6
Initial D1 (cm/s – ml/min)	17.5–0.44	18.8–0.44	16.1–0.45	18.8–0.44	20.0–0.44	16.1–0.41
Final D1	–	–	11.6–0.23	–	–	11.6–0.22
Initial D2 (cm/s – ml/min)	144–7.8	163–7.8	122–7.8	144–6.8	163–6.8	134–7.6
Final D2	–	–	184–7.8	–	–	196–7.6
Initial ALV _{acc} (cm/s – ml/min)	2.7–0.44	3.0–0.44	2.4–0.45	3.1–0.44	3.3–0.44	2.5–0.41
Final ALV _{acc}	–	–	1.8–0.23	–	–	1.8–0.22
Initial ALV _{inj} (cm/s – ml/min)	48.5–7.8	53.2–7.8	42.4–7.8	47.5–6.8	52.1–6.8	45.5–7.6
Final ALV _{inj}	–	–	58.3–7.8	–	–	60.2–7.6

nearby He discharge zone. The separation of the discharge chamber, from the secondary ionization zone, along with the use of a counter-current He gas flow, guarantees that only pure He passes through the discharge chamber, limiting the possibility of contamination [3].

To the best of the present authors' knowledge, only a single GC × GC-DHID research (using cryogenic modulation) has been described [4]. Specifically, Winniford *et al.* used a miniaturized pulsed discharge detector (acquisition frequency: 100 Hz) in photoionization modes for universal and selective detection. Mixtures of alkanes and aromatic compounds were used to evaluate the detector performance. The authors affirmed that extra-column band broadening was 20% ± 5% more compared to an FID, while sensitivity was similar.

The present investigation is based on the use, as detection system, of a recently-developed DHID in flow modulation (FM) GC × GC experiments. The novel device is defined as barrier discharge ionization detector (BID), with such a definition from here onwards used [5]. The FM approach applied is based on that introduced by Seeley [6] (later corroborated by Amirav [7]), even though with reduced gas flow requirements [8]. The analytical results attained were directly compared with FID-derived ones, in terms of extra-column band broadening, sensitivity and dynamic range. Moreover, BID parameters such as acquisition frequency and discharge flow were finely tuned. Applications were carried out by using a series of standard compounds characterized by different chemical classes, along with a sample of diesel fuel. Particular emphasis was devoted to the evaluation of the BID performance in relation to saturated and aromatic hydrocarbons, for a possible future use of the FM GC × GC-BID instrumentation for the evaluation of food contamination. In fact, the presence of mineral oil saturated and aromatic hydrocarbons (MOSH/MOAH) in foods has been subjected to increasing analytical attention in recent years [9–11]. In such application-types, a high performance liquid chromatography sample-preparation step is commonly used prior to GC-FID analysis. The use of the FID is useful for the straightforward quantification of both MOSH and MOAH classes. Recently, the use of GC × GC-FID has started to appear in such research due to its enhanced resolving power and sensitivity [10,11].

2. Materials and methods

2.1. Samples and sample preparation

C₉–C₁₀ *n*-alkanes, ethyl- and pentylbenzene, 2-phenylethanol and 1-nonanol, octanal and α -ionone, C_{16:0} and C_{18:1} fatty acid methyl esters (FAMES) were supplied by Sigma-Aldrich/Supelco (Bellefonte, PA, USA). Solutions were prepared in *n*-hexane.

A diesel fuel sample was attained from a local petrochemical station, and was injected neat.

2.2. FM GC × GC-BID/FID analyses

All comprehensive two-dimensional GC-BID applications were carried out on a system consisting of a Shimadzu GC Tracera instrument (Kyoto, Japan), equipped also with an FID system. A description of the BID system is available [5]. A He purifier (VICI Valco Instruments, Houston, TX, USA) was used to reduce carrier gas impurities. Data were acquired by using the GCsolution software ver. 2.42 (Shimadzu). Bidimensional chromatograms were generated by using the ChromSquare software ver. 2.2 (Shimadzu). The GC was equipped with an AOC-20i auto-injector, and a split-splitless injector.

The primary column was: SLB-5 ms [(silphenylene polymer, practically equivalent in polarity to poly(5% diphenyl/95% methylsiloxane))] 20 m × 0.18 mm ID × 0.18 μ m *d_f*. The secondary column was: SPB-50 [poly(50% diphenyl/50% dimethyl siloxane)] 5 m × 0.32 mm ID × 0.20 μ m *d_f*. Both columns were supplied by Sigma-Aldrich/Supelco.

Flow modulation was performed following the model proposed by Seeley [6]. Briefly, the modulator was constructed by using two MXT Y-unions (Restek Corporation, Bellefonte, PA, USA) and a 2-way solenoid valve (located outside the GC), connected to an auxiliary pressure source. The output ports of the solenoid valve were connected to the unions by using two metallic branches. One of the Y-unions was linked to the primary-column outlet, while the other directed the flow to the second dimension. A stainless steel accumulation loop measuring 20 cm × 0.51 mm ID (SGE, Ringwood, Victoria, Australia) bridged the two Y-unions. Modulation period was 4500 ms, with a 600 ms flushing period.

Both detectors were maintained at a temperature of 310 °C. The injector in all applications was maintained at a temperature of 310 °C. BID and FID acquisition frequency was 250 Hz in all applications. Optimized BID discharge He flow: 70 ml/min. FID gas flows: H₂: 40 ml/min; make-up (He): 40 ml/min; air: 400 ml/min.

Table 2

Peak widths (4 σ) of alkanes (C_{9–10}) and FAMES (C_{16:0–18:1}) in GC × GC-BID (at different discharge flows) and GC × GC-FID applications (*n* = 3). Peak widths are expressed in ms.

	GC × GC-BID		GC × GC-FID
	55 ml/min	70 ml/min	
C ₉	550	480	460
C ₁₀	470	430	450
C _{16:0}	700	660	650
C _{18:1}	1210	1170	1150

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