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Article

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A Gas Chromatography Method for Simultaneous Quantification of Inorganic Gases and Light Hydrocarbons Generated in Thermochemical Processes

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This paper reports a method for simultaneous determination of H_2, O_2, N_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4 (propadiene and propyne), C_3H_6, C_3H_8 and C_4H_{10} (*n*-butane and isobutane) by gas chromatography using thermal conductivity and flame ionization detectors. A single porous layer open tubular column (0.53 mm internal diameter × 30 m length × 30 µm thick) was applied and no catalytic converter was needed to convert CO and CO_2 into CH_4 to enable identification by a flame ionization detector. The most appropriate chromatographic conditions were defined for the method and it was validated according to the recommendations of the National Health Surveillance Agency and the National Institute of Metrology, Standardization and Industrial Quality. Chromatographic conditions defined for the target gases presented satisfactory linearity (r > 0.99), and limits of detection ranged between 0.0916 and 2.75 ppm. High accuracy (98-101%) obtained for the gas chromatography/thermal conductivity detector/flame ionization detector method associated to low relative standard deviation (< 2%) confirmed its applicability in routine quantification of target gases formed during the pyrolysis of municipal refuse-derived fuel.

Keywords: combustible gases, flame ionization detector, municipal solid waste, synthesis gases, thermal conductivity detector

Introduction

Thermochemical processes (pyrolysis and gasification) constitute alternatives to minimize and convert refuse-derived fuel (RDF) from municipal solid waste (MSW, also known as municipal refuse-derived fuel (MRDF)) into energy. Inorganic gaseous compounds (CO, CO_2, H_2, N_2, O_2, etc.) and light hydrocarbons (C_1-C_6) are generated as products of these processes.[1,2] Some of these gases are combustible (CO, H_2 and C_1-C_6) and may be used for energy production, thus adding value to the application of thermochemical processes.

The composition and proportion of gases formed during thermochemical processes vary according to the type of waste, reactor, and operational conditions, such as temperature and heating rate.[3-5] As some of these gases may be used as alternative energy sources, it is critical to develop methodologies to enable simultaneous characterization and quantification of all gases formed during thermochemical treatment.

Table 1 summarizes chromatographic conditions applied in standard methods (ASTM D3612-02, methods A and C)[6] and by Supelco[7] to quantify inorganic gases (H_2, O_2, N_2, CO and CO_2) and light hydrocarbons (C_1-C_4) by thermal conductivity (TCD) and flame ionization (FID) detectors, respectively.[6,7] ASTM D3612-02 (method A) requires two columns connected in series (a molecular sieve and a Poparak N columns) to separate and identify the inorganic gases and light hydrocarbons. Besides, a catalytic converter (methanizer) is needed to convert CO and CO_2 into CH_4 for detection by FID under acceptable sensitivity using argon as carrier gas. Other limitations of this method are: (*i*) light hydrocarbons propane and propylene are not separated under the furnished conditions;

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Table 1. Traditional conditions for monitoring inorganic gases and light hydrocarbons (C_1-C_4) by gas chromatography

Analytes	Chromatographic conditions					Carrier gas (flow rate / (mL min^{-1}))	Reference
	Column	Detector	Temperature				
			Injector / °C	Detector / °C	Oven		
H_2, O_2, N_2, CO, CO_2, C_1-C_2 and C_4H_{10}	molecular sieve Porapak N	TCD/methanizer/ FID	200	150 (TCD) 300 (FID)	35 °C (8 min), rate of 20 °C min^{-1} up to 132 °C (15.5 min), rate of 25 °C min^{-1} up to 150 °C run time: 30 min	Ar (30)	6
H_2, O_2, N_2, CO, CO_2, C_1-C_2, C_3H_8	molecular sieve Carboxen-1006 PLOT	TCD/methanizer/ FID	200	250 (TCD) 350 (FID)	40 °C (3 min), rate of 24 °C min^{-1} up to 170 °C (2 min), rate of 24 °C min^{-1} up to 250 °C (5 min) run time: 16 min	Ar (12)	6
H_2, O_2, N_2, CO, CO_2 and C_1-C_2	Carboxen-1010 PLOT	TCD/methanizer/ FID	200	230	35 °C (7.5 min), rate of 24 °C min^{-1} up to 250 °C run time: 27 min	Ar (3.0)	7
CO_2, C_1-C_2, C_3H_8 C_3H_4 (propyne), C_3H_6 and *n*-C_4H_{10}	Carboxen-1006 PLOT	TCD	200	230	35 °C (1.0 min), rate of 24 °C min^{-1} up to 250 °C run time: 17 min	He (10)	7

PLOT: porous layer open tubular; TCD: thermal conductivity detector; FID: flame ionization detector; He: helium; Ar: argon.

(*ii*) C_3H_4 (propadiene and propyne) are not targeted by this method, and (*iii*) it enables the identification of butane only (it is not clear if is *n*- or isobutane).[6] The second standard test method is ASTM D3612-02 (method C) which enables the analysis of these target gases by also employing two columns connected in series (a molecular sieve and a porous layer open tubular (PLOT) column (Carboxen-1006)), a methanizer and argon as a carrier gas. However, light hydrocarbons (C_3H_4 (propyne and propadiene), C_3H_6 and C_4H_{10} (*n*- and isobutane)) are not evaluated in this method.[6]

On the other hand, a method using a single column (Carboxen-1010 PLOT or Carboxen-1006 PLOT) and argon or helium as carrier gases were proposed by Supelco.[7] The proposed method applies Carboxen-1010 PLOT column, argon as carrier gas, FID and TCD detectors and a methanizer, yet no hydrocarbons containing 3 or 4 carbon atoms were evaluated. Although it is possible to analyze C_3H_4 (propyne), C_3H_6, C_3H_8 and C_4H_{10} (*n*-butane) by the method proposed by Supelco, light hydrocarbons such as C_3H_4 (propadiene) and C_4H_{10} (isobutane) as well as inorganic gases (H_2 and O_2) were not evaluated by this method. Furthermore, the method does not present a complete and effective separation of CO and N_2 analytes. In addition, no details regarding method validation such as: linear range, linearity, repeatability (intra-day and inter-day studies), limits of detection (LOD) and quantification (LOQ) were presented in Supelco studies.[7]

These evidences demonstrate that it is critical to perform more studies involving the use of Carboxen-1010 PLOT, which is a more efficient column for the separation of inorganic gases and light hydrocarbons up to 3 carbon atoms. The use of helium rather than argon as carrier gas must also be evaluated as it shows better performance for TCD due to higher thermal conductivity and response factor.[8] The combination of these two factors may lead to the development of a single method for separation, identification and quantification of inorganic gases and light hydrocarbons.

This work proposes a new chromatographic method which covers a broader scope of analytes when compared to ASTM D3612-02 (methods A and B)[6] and Supelco[7] methods. The new method was developed and validated aiming the simultaneous quantification of inorganic gases (CO, CO_2, H_2, N_2, O_2) and light hydrocarbons (C_1-C_3 and C_4H_{10} (*n*-butane and isobutane)) by using a single column (Carboxen-1010 PLOT) helium as carrier gas, and detection via TCD and FID without the need for a methanizer. Besides, the procedure was also applied for the identification of inorganic gases and light hydrocarbons generated during the pyrolysis of real MRDF.

Experimental

Reagents

Helium (He), hydrogen (H_2), oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2), methane (CH_4), propane (C_3H_8) (99.999% v/v); carbon monoxide (CO) (10% v/v); propene (C_3H_6) (99.555% v/v); ethyne (C_2H_2) (99.888% v/v); ethane (C_2H_6) (19.960% v/v); ethene (C_2H_4) (20.090% v/v); propadiene (C_3H_6) (20.190% v/v); propyne (C_3H_4) (19.880% v/v); *n*-butane (*n*-C_4H_{10}) (9.929% v/v) and isobutane (*iso*-C_4H_{10}) (9.958% v/v) were all obtained from White Martins (Osasco, Brazil) and used as purchased.

MRDF sample

MRDF (with 15 wt.% moisture content) was produced in an industrial solid waste processing line (SWPL) as detailed previously by Infiesta *et al.*[9] by using MSW generated in the city of Boa Esperança, Minas Gerais, Brazil. MSW is pretreated by mechanical processes such as selection, crushing and drying in this SWPL. The mass balance of the SWPL (4148 kWh), lower heating values (LHV) of the MSW (9.3 MJ kg^{-1}) and MRDF (15.8 MJ kg^{-1}), as well as average characterization of the MRDF produced from MSW were all determined in the previous study.[9]

Chromatographic conditions

Chromatographic analyses were performed by using a gas chromatographer (GC) (Shimadzu GC-2014, Kyoto, Japan) equipped with TCD and FID detectors, respectively, which were operated in series. Data were processed using the GC-Solution software. A Carboxen 1010 PLOT column (0.53 mm internal diameter × 30 m long × 30 µm thick) was used as stationary phase.

Helium (12.9 mL min^{-1}) was used as carrier gas. Synthetic air and hydrogen were combined to generate the FID flame. Inorganic gases (H_2, N_2, O_2, CO and CO_2) and hydrocarbons (CH_4, C_2H_2, C_2H_6, C_2H_4, C_3H_6, C_3H_8, C_3H_4 (propadiene and propyne), iso-C_4H_{10} and *n*-C_4H_{10}) were detected by TCD and FID, respectively.

Method validation

Analytical curves and linearity

Method linearity was evaluated by developing calibration curves with data obtained from the injection of 5-10 different concentrations (ranged from 0.0916 to 274 ppm, and prepared in triplicate) of each analyte.[10-13]

Tedlar bags of polyprolyene (1 L, CEL Scientific Corporation, Cerritos, USA) were used to transfer the sample of each isolated analyte from the cylinders to the atmospheric pressure. Dilution of gases was performed by adding argon gas to each analyte directly by using a suitable microsyringe (fixed needle, Teflon tip and capacity of 1000 µL) for collecting gas samples (Hamilton Gastight 1001, Nevada, USA).

The concentration of each analyte was calculated considering the volume of gas in the temperature of 0 °C to facilitate the comparison with the results obtained with ASTM D3612-02 (methods A and C).[6]

Selectivity

Method selectivity was calculated considering the resolution (R_s) between the different target compounds by using retention times, and base width of the peak for each compound (equation 1):

$$R_s = \frac{2 \times (t_{rA} - t_{rB})}{wA + wB} \quad (1)$$

where t_{rA}: retention time of compound A; t_{rB}: retention time of compound B; wA: base width of peak A; wB: base width of peak B.

LOD and LOQ

LOD and LOQ were calculated for each target compound by using the signal-to-noise ratio method (LOD = 3:1 and LOQ = 10:1, signal-to-noise ratio, respectively).[6,14,15]

Precision

Both intra-day and inter-day precision were assessed for the mixture of different concentrations of analytes prepared in triplicates in three different concentrations. Three separate bags were prepared with the mixture for the three evaluated concentrations (low, medium and high), and the linear range obtained for each compound was checked as shown in Table S1 (Supplementary Information (SI) section). Subsequently, the mixture of each bag was injected only once for each concentration under analysis.

For the evaluation of intra-day precision (repeatability), samples were injected in the GC/TCD/FID four times within intervals of 2 h (1, 3, 5 and 7 h). Inter-day precision (reproducibility) was evaluated by injecting sample in over 5 different days (1, 3, 7, 15 and 30 days). The relative standard deviations (RSD, in percentage) were determined as according to data obtained during these runs.

Method application

A laboratory scale pyrolysis reactor (50 mL) (Figure S1, SI section) was used for the production of synthesis gases from MRDF. Initially, 20.1 g of MRDF were inserted into the reactor. The reactor was heated externally by using an electrical resistance coupled to a temperature controller (up to 900 ºC).[16,17] Condensable gases generated during the pyrolysis process were retained in the condenser, and non-condensable gases were collected in the combustion cylinder. After a pressure of 8 bar was reached, generated gases were extracted from the combustion cylinder (Figure S1) by using Tedlar bags, and kept at rest for 15 min to reach room temperature and pressure. Then, sample were injected in the GC/TCD/FID.

Accuracy

Method accuracy was evaluated by assessing analyte recovery in the synthesis gas generated in the pyrolysis of real MRDF. Three samples prepared in triplicates, were fortified by adding different concentrations of the analytes (low, medium and high) within the linear range obtained for each one (Table S1). The determined concentration of fortified samples was divided by the theoretical concentration of the fortified samples to assess recovery (equation 2):

$$\text{Recovery} = \frac{C1}{C2} \times 100 \quad (2)$$

where C1: experimental concentration of analyte in the fortified sample; C2: theoretical concentration of analyte in the fortified sample.

Results and Discussion

Evaluation of chromatographic conditions and method validation

Table 2 presents all chromatographic conditions tested in this study. The most appropriate conditions of operation were selected according to signal intensity associated to the detection and selectivity of target compounds.

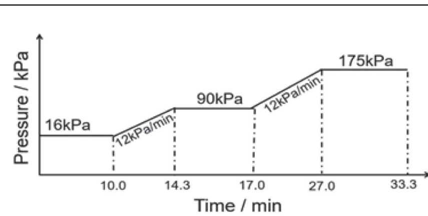
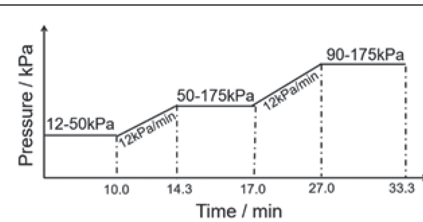
Figure 1 shows the chromatographic profile of the analyte mixture under the best chromatographic conditions.

R_s values presented in Table 3 were calculated by using equation 1. R_s values greater than 1.5 were obtained for the following analytes: H_2/O_2, N_2/CO, CO/CO_2, CH_4/C_2H_2, C_2H_2/C_2H_4, C_2H_4/C_2H_6, C_2H_6/C_3H_4 (propyne), C_3H_8/iso-C_4H_{10} and iso-C_4H_{10}/*n*-C_4H_{10}, thus indicating a separation of 100% between the peaks of each of these analytes.[8] R_s values between 1.18-1.38 were obtained for O_2/N_2, C_3H_4 (propadiene)/C_3H_4(propyne), C_3H_4(propyne)/C_3H_6 and C_3H_6/C_3H_8, indicating an overlap of only 2% between peaks.[8] These results demonstrate the appropriate selectivity of the proposed GC/TCD/FID method.

Method linearity (represented by the correlation coefficient, r) is shown in Table 4, and was determined by using calibration curves. High linearity was obtained for all analytes (r values > 0.99) and comply with requirements of the National Health Surveillance Agency (ANVISA)[14] and the National Institute of Metrology, Standardization and Industrial Quality (INMETRO)[15] (Brazil).

LOD values determined by the signal-to-noise ratio were compared with those reported for ASTM D3612-02 (methods A and C)[6] (Table 4). Lower LOD values were obtained for the present study when compared to ASTM D3612-02 (method A). Depending on the analyte, the proposed method enables the detection of concentrations ranging from 546 times lower for N_2 and O_2 to 34 times lower for CO and CO_2, 11 times lower for CH_4, C_2H_2, C_2H_4 and C_2H_6, and 1.8 times lower for H_2. On the other hand, with the exception of N_2 and O_2, lower LOD values are reported for ASTM D3612-02 (method C). It was

Table 2. Chromatographic conditions tested and established for the GC/TCD/FID method developed for the quantification of inorganic gases and light hydrocarbons

Parameter	Evaluated range	Established values
Detector temperature (FID and TCD) / °C	200 and 250	250
Oven temperature	35 °C (10 min), rates of 12, 24, 48 and 60 °C min^{-1} up to 240 °C	35 °C (10 min), rate of 48 °C min^{-1} up to 240 °C
Injector temperature / °C	200	200
Injection mode	split and splitless	split
Split ratio	1:10 to 1:20	1:15
Carrier gas	He or Ar	He
Flow control mode	linear velocity or pressure 16 kPa (10 min), rates of 12, 24, 48 and 60 °C min^{-1} up to 240 °C	linear velocity
Pressure / kPa	 	

TCD: thermal conductivity detector; FID: flame ionization detector; He: helium; Ar: argon.

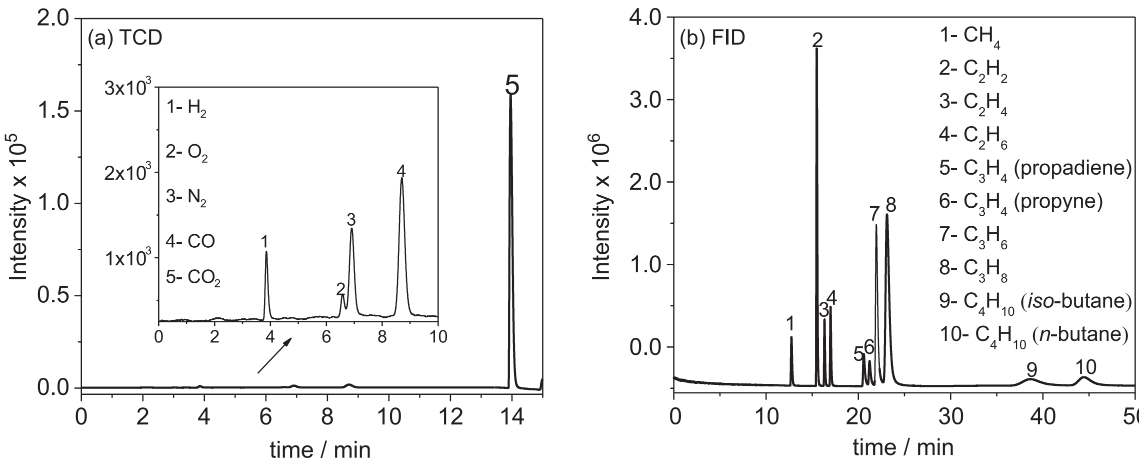


Figure 1. (a) TCD chromatograms and (b) FID obtained from the mixture of inorganic gases and light hydrocarbons under the best chromatographic conditions.

Table 3. R_s values calculated for each pair of analytes in accordance with their sequential elution using the most appropriate conditions of the GC/TCD/FID method

Pair of analytes	R_s
H_2/O_2	10.1
O_2/N_2	1.18
N_2/CO	3.36
CO/CO_2	10.5
CH_4/C_2H_2	8.42
C_2H_2/C_2H_4	2.97
C_2H_4/C_2H_6	1.90
$C_2H_6/C_3H_4{}^a$	8.66
$C_3H_4{}^a/C_3H_4{}^b$	1.38
$C_3H_4{}^b/C_3H_6$	1.26
C_3H_6/C_3H_8	1.37
C_3H_8/iso-C_4H_{10}	7.24
iso-C_4H_{10}/*n*-C_4H_{10}	1.92

[a]Propadiene; [b]propyne. R_s: resolution.

not possible to compare the LOQ values obtained in the proposed method with values obtained by ASTM D3612-02 since no LOQ values are presented for methods A and C. Besides, as previously described in the Introduction section, the ASTM D3612-02 (method C) requires the use of two columns connected in series (a molecular sieve and a Carboxen-1006 PLOT columns) and a methanizer to convert CO and CO_2 to CH_4 for acceptable sensitivity by using argon as carrier gas via detection by FID. In addition, light hydrocarbons (C_3H_4 (propyne and propadiene), C_3H_6 and C_4H_{10} (*n*- and isobutane)) are not within the scope of method C.[6]

It can also be observed in this work that H_2 presented the higher LOD value when compared to the other inorganic gases and light hydrocarbons (Table 4). This can be justified by the proximity between heat capacity values pertaining to helium and hydrogen, thus generating a reduced difference on TCD signal.

RSD values obtained for target gases for inter (between 0.31 and 1.3%) and intra-day reproducibility tests (between 0.76 and 2.0%) (Tables S2 and S3, SI section) were lower than 2%, while higher RSD values (between 3 and 13%) were reported for ASTM D3612-02 (method C). These results show low variability between measurements obtained for each replicate made within a day or in different days, which guarantees the reliability of results obtained by the application of the proposed method.

Application of the method under the best chromatographic conditions for determination of syngas characterization during pyrolysis of MRDF

Figure 2 shows the chromatogram obtained from the syngas generated during the pyrolysis of MRDF.

According to data obtained by GC, MRDF is composed by the following constituents (%, v/v) in a decreasing order: CH_4 (24.9 ± 1.7) > CO_2 (24.0 ± 1.0) > CO (17.2 ± 1.6) > C_2H_6 (8.0 ± 0.5) > C_3H_6 (6.2 ± 0.1) > C_2H_4 (5.9 ± 0.2) > C_3H_8 (2.8 ± 0.3) > *n*-C_4H_{10} (2.7 ± 0.3) > N_2 (5.8 ± 0.2) > iso-C_4H_{10} (1.6 ± 0.8) > O_2 (1.0 ± 0.3). A LHV of 25.5 ± 1.7 MJ Nm^{-3} was calculated by using these results and as according to ASTM 5865-13[18] (Table 5).

The LHV (25.5 ± 1.7 MJ Nm^{-3}) of the synthesis gas is equivalent to values reported for oily sludge (23.5 ± 4.3 MJ Nm^{-3})[19] (Table 5). On the other hand, the present LHV obtained for the synthesis gas via pyrolysis of MRDF is higher than the LHV obtained for pyrolysis of sewage sludge (9.5 ± 0.3 MJ Nm^{-3}),[10] rice straw (11.6 ± 0.2 MJ Nm^{-3}),[11] leather-tannery waste (6.0 ± 6.0 MJ Nm^{-3}),[12] and horse manure biowaste (13.9 ± 1.8 MJ Nm^{-3}).[13] Gasification process applied to the same matrix (MRDF), also resulted in synthesis gases which presented an inferior LHV (between 5.5 and 17.0 ± 4.7 MJ Nm^{-3}) (Table 5).[20-22] On the basis of these

Table 4. Evaluated range, linear range, linearity (r), and limits of detection (LOD) and quantification (LOQ) obtained for each analyte identified in the proposed method compared to literature[6]

Analyte	Evaluated range / ppm	Linear range / ppm	Linearity (r)	LOD[a] / ppm	LOD[b] / ppm	LOD[c] / ppm	LOQ[d] / ppm
H_2	2.75 to 210	8.96 to 210	0.99309	2.75	5	0.6	8.96
N_2	0.0916 to 101	0.314 to 101	0.99995	0.0916	50	11.2	0.314
O_2	0.0916 to 101	0.314 to 101	0.99979	0.0916	50	11.0	0.314
CO	0.732 to 82.8	2.46 to 82.8	0.99725	0.732	25	0.09	2.46
CO_2	0.732 to 270	2.46 to 270	0.99697	0.732	25	0.1	2.46
CH_4	0.0916 to 274	0.314 to 274	0.99811	0.0916	1	0.06	0.314
C_2H_2	0.0916 to 210	0.314 to 210	0.99962	0.0916	1	0.05	0.314
C_2H_4	0.0916 to 224	0.314 to 224	0.99964	0.0916	1	0.04	0.314
C_2H_6	0.0916 to 224	0.314 to 224	0.99960	0.0916	1	0.04	0.314
C_3H_4[e]	0.0916 to 193	0.314 to 193	0.99978	0.0916	–	–	0.314
C_3H_4[f]	0.0916 to 193	0.314 to 193	0.99692	0.0916	–	–	0.314
C_3H_6	0.0916 to 210	0.314 to 210	0.99943	0.0916	–	–	0.314
C_3H_8	0.0916 to 210	0.314 to 210	0.99919	0.0916	–	0.2	0.314
iso-C_4H_{10}	1.83 to 193	6.05 to 193	0.99511	1.83	–	–	6.05
n-C_4H_{10}	3.67 to 224	12.1 to 224	0.99889	3.67	–	–	12.1

[a]LOD of the present work; [b]LOD of the ASTM D3612-02 (method A); [c]LOD of the ASTM D3612-02 (method C); [d]LOQ of present work; [e]propadiene; [f]propyne.

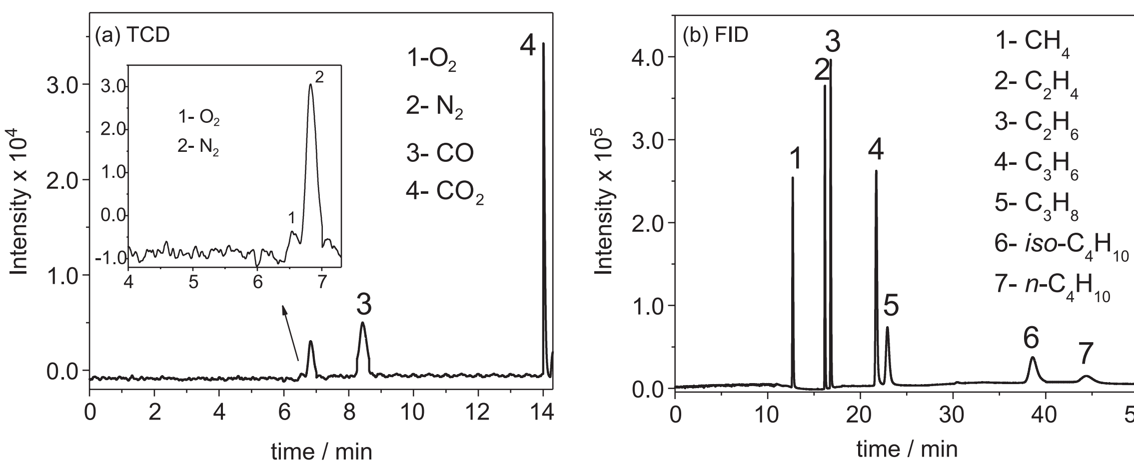


Figure 2. Chromatograms obtained for the analysis of the synthesis gas generated from pyrolysis of real MRDF using (a) TCD and (b) FID detectors under the best chromatographic conditions.

results, the increased LHV obtained for the synthesis gas analyzed by pyrolysis of MRDF in this study is justified by the high concentration of hydrocarbons (ΣC1-C4 = 52.1% v/v) and absence of H_2 in the sample (Table 5).

Finally, the accuracy of the GC/TCD/FID method was evaluated by recovery tests performed before and after spike of samples containing known concentrations of target gases. Recovery values ranged from 98 to 101% (Table 6) and are in accordance with recommendations made by INMETRO (between 98 and 102%).[15] In addition, these results indicate the absence of matrix interference. Hence, the proposed chromatographic method may be considered as adequate for the accurate measurement of each analyte in the method.

Conclusions

A GC/TCD/FID method was developed and validated for the simultaneous quantification of inorganic gases and light hydrocarbons by gas chromatography using a single Carboxen 1010 PLOT column. The proposed method complies with standards recommended by ANVISA and INMETRO. As the proposed method was successfully applied for characterization of the synthesis gas generated during the pyrolysis of real MRDF, it is useful for the identification and quantification of combustible gases generated during thermal processes applied as waste treatment alternatives and which may be explored as energy source. Therefore, the present work supports the use of GC/TCD/FID as a straightforward solution for routine quantification of inorganic gases and

Table 5. Comparison of synthesis gases obtained from different types of matrices using pyrolysis or gasification processes

Matrix	LHV / (MJ Nm^{-3})	Temperature / °C	Composition (v/v) / %	Reference
MRDF[a]	25.5 ± 1.7	900	CH_4 (24.9 ± 1.7) > CO_2 (24.0 ± 1.0) > CO (17.2 ± 1.6) > C_2H_6 (8.0 ± 0.5) > C_3H_6 (6.2 ± 0.1) > C_2H_4 (5.9 ± 0.2) > C_3H_8 (2.8 ± 0.3) > n-C_4H_{10} (2.7 ± 0.3) > N_2 (5.8 ± 0.2) > iso-C_4H_{10} (1.6 ± 0.8) and O_2 (1.0 ± 0.3)	present work
Sewage sludge[a]	9.5 ± 0.3	450	H_2 (13.3 ± 1.3), CO (18.7 ± 2.1), CO_2 (30.1 ± 7.6), CH_4 (2.28 ± 0.2), C_2H_2 (0.03 ± 0.04), C_2H_4 (0.680 ± 1.0), C_2H_6 (0.3 ± 0.2), C_3H_6 (1.0 ± 0.1) and C_3H_8 (2.6 ± 0.7)	10
Rice straw[a]	11.6 ± 0.2	550	H_2 (5.0 ± 0.0), CO (23.5 ± 1.6), CO_2 (52.0 ± 0.4) and CH_4 (13.3 ± 1.2)	11
Leather-tannery waste[a]	6.0 ± 6.0	300-500	H_2 (17.5 ± 16), CO (15.1 ± 3.3), CO_2 (34.4 ± 5.7) and CH_4 (5.5 ± 4.6)	12
Horse manure biowaste[a]	13.9 ± 1.8	450-650	H_2 (1.0 ± 0.8), CO (70.0 ± 8.3), CO_2 (22.0 ± 4.8) and CH_4 (23.0 ± 4.5)	13
Oily sludge[a]	23.5 ± 4.3	500	H_2 (43.3), CO (4.0), CO_2 (3.0) and C1-C3 (44.2)	19
RDF[b]	9.9 ± 1.0	1127-1327	H_2 (36.0 ± 10.1), CO (42.0 ± 6.8), CO_2 (8.0 ± 7.5) and CH_4 (3.6 ± 1.1)	20
MSW[b]	5.5	850	H_2 (27.8), CO (20.1), CO_2 (7.4), N_2 (44.7)	21
MSW[b]	17.0 ± 4.7	900	H_2 (37.0 ± 11.4), CO (22.0 ± 6.2), CO_2 (14.0 ± 13.3), CH_4 (11.5 ± 3.2) and C3-C4 (11.0 ± 6.3)	22

[a]Pyrolysis process; [b]gasification process. LHV: lower heating value; MRDF: municipal refuse-derived fuel; RDF: refuse-derived fuel; MSW: municipal solid waste.

Table 6. Recovery of the analytes studied by the proposed chromatographic method developed for simultaneous analysis of inorganic gases and light hydrocarbons generated in thermochemical processes

Analyte	Concentration / ppm	Recovery / %	Analyte	Concentration / ppm	Recovery / %	Analyte	Concentration / ppm	Recovery / %
	0.560	98.5 ± 0.3		0.560	99.7 ± 1.3		0.560	98.4 ± 1.7
O_2	4.48	98.3 ± 0.6	CH_4	10.1	98.2 ± 0.7	C_3H_4[a]	10.1	99.6 ± 0.8
	78.4	99.7 ± 0.3		202	99.0 ± 1.2		168	99.6 ± 0.4
	11.2	98.4 ± 0.5		0.560	98.6 ± 0.8		0.560	98.4 ± 1.3
H_2	101	99.3 ± 0.8	C_2H_2	10.1	99.4 ± 0.4	C_3H_6	10.1	99.6 ± 1.3
	190	99.7 ± 0.6		190	100 ± 0.8		190	100 ± 1.7
	0.560	98.0 ± 0.2		0.560	98.6 ± 0.8		0.560	98.4 ± 1.3
N_2	4.48	98.6 ± 1.6	C_2H_4	10.1	99.1 ± 0.5	C_3H_8	10.1	99.4 ± 1.5
	78.4	99.2 ± 0.6		202	99.6 ± 1.0		190	98.4 ± 1.1
	5.60	98.5 ± 0.6		0.560	98.2 ± 0.5		8.96	99.6 ± 0.7
CO	31.4	101 ± 0.8	C_2H_6	10.1	100 ± 1.0	iso-C_4H_{10}	56	98.4 ± 1.3
	56.0	99.8 ± 0.3		202	99.3 ± 0.5		168	99.8 ± 0.5
	5.60	98.1 ± 0.3		0.560	98.6 ± 1.2		14.6	98.3 ± 0.7
CO_2	101	98.7 ± 1.2	C_3H_4[b]	10.1	99.6 ± 0.8	n-C_4H_{10}	101	99.3 ± 0.3
	190	100 ± 0.7		168	100 ± 1.2		202	98.5 ± 0.8

[a]Propyne; [b]propadiene.

light hydrocarbons generated in thermochemical treatment processes using different matrices.

Supplementary Information

Supplementary information (schematic representation of the laboratory scale pyrolysis system, concentrations of the analytes evaluated in precision and accuracy tests and, concentrations and relative standard deviation values used in intra-day and inter-day precision) is available free of charge at http://jbcs.sbq.org.br as PDF file.

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Author Contributions

Valdislaine M. Silva was responsible for conceptualization, methodology, validation, formal analysis, investigation, visualization, writing-original draft and writing-review and editing; José S. Pessoa Filho for methodology, formal analysis and investigation; Raquel M. F. Souza for conceptualization, methodology, investigation, visualization, supervision, writing-original draft and writing-review and editing; Solidônio R. Carvalho for term, conceptualization, resources, supervision, funding acquisition, writing-original draft and writing-review and editing. Valério L. Borges and Cassius R. N. Ferreira were responsible for conceptualization, resources and funding acquisition. Maria Clara V. M. Starling was responsible for conceptualization, formal analysis, writing-original draft and writing-review and editing; Alam G. Trovó for term, conceptualization, methodology, validation, formal analysis, investigation, resources, writing-original draft and writing-review and editing, visualization, supervision, project administration and funding acquisition.

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