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 H₂, O₂, N₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₄ (propadiene and propyne), C₃H₆, C₃H₈ and C₄H₁₀ (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 CO₂ into CH₄ 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, CO₂, H₂, N₂, O₂, etc.) and light hydrocarbons (C₁-C₄) are generated as products of these processes. Some of these gases are combustible (CO, H₂ and C₁-C₄) 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. 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) and by Supelco to quantify inorganic gases (H₂, O₂, N₂, CO and CO₂) and light hydrocarbons (C₁-C₄) by thermal conductivity (TCD) and flame ionization (FID) detectors, respectively. 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 CO₂ into CH₄ 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;
Table 1. Traditional conditions for monitoring inorganic gases and light hydrocarbons (C₁-C₄) by gas chromatography

| Analytes                      | Column Detector | Temperature                | Carrier gas (flow rate / (mL min⁻¹)) | Reference |
|-------------------------------|-----------------|----------------------------|--------------------------------------|-----------|
|                               | Column          | Oven                       |                                      |           |
|                               |                  | Injector / °C | Detector / °C | Oven run time: 17 min | Ar (10) | 7 |
| H₂, O₂, N₂, CO, CO₂, C₂H₆, C₃H₄ | molecular sieve | 200 | 250 (TCD) | 35 °C (7.5 min), rate of 24 °C min⁻¹ up to 250 °C | He (10) | 7 |
|                               | TCD/methanizer/ FID | 350 (FID) | 230 | 35 °C (1.0 min), rate of 24 °C min⁻¹ up to 250 °C run time: 27 min |          |   |
| H₂, O₂, N₂, CO, CO₂, C₃H₆, C₄H₁₀ | molecular sieve | 200 | 300 (TCD) | 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 |
|                               | TCD/methanizer/ 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 | 24 °C min⁻¹ up to 250 °C |          |   |
| H₂, O₂, N₂, CO, CO₂, C₃H₈, C₄H₁₀ | Carboxen-1010 PLOT | 200 | 250 (TCD) | 35 °C (7.5 min), rate of 24 °C min⁻¹ up to 250 °C run time: 27 min | Ar (12) | 6 |
|                               | TCD/methanizer/ FID | 350 (FID) | 230 | 35 °C (7.5 min), rate of 24 °C min⁻¹ up to 250 °C run time: 27 min |          |   |

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

(ii) C₄H₁₀ (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). 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 (C₃H₄ (propyne and propadiene), C₃H₆ and C₄H₁₀ (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 C₃H₄ (propyne), C₄H₁₀, C₃H₆ and C₄H₁₀ (n-butane) by the method proposed by Supelco, light hydrocarbons such as C₃H₄ (propadiene) and C₄H₁₀ (isobutane) as well as inorganic gases (H₂ and O₂) were not evaluated by this method. Furthermore, the method does not present a complete and effective separation of CO and N₂ 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. 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) and Supelco methods. The new method was developed and validated aiming the simultaneous quantification of inorganic gases (CO, CO₂, H₂, N₂, O₂) and light hydrocarbons (C₁-C₃ and C₄H₁₀ (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 (H₂), oxygen (O₂), nitrogen (N₂), carbon dioxide (CO₂), methane (CH₄), propane (C₃H₈) (99.999% v/v); carbon monoxide (CO) (10% v/v); propene (C₃H₆) (99.555% v/v); ethyne (C₂H₂) (99.888% v/v), ethene (C₂H₄) (19.960% v/v); ethyne (C₂H₂) (20.090% v/v); propadiene (C₄H₁₀) (20.190% v/v); propyne (C₃H₄) (19.880% v/v), n-butane (C₄H₁₀) (9.929% v/v) and isobutane (iso-C₄H₁₀) (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. 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.

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\(_2\)H\(_2\), C\(_2\)H\(_6\), C\(_3\)H\(_6\), C\(_3\)H\(_8\), C\(_3\)H\(_4\) (propadiene and propyne), iso-C\(_4\)H\(_10\) and n-C\(_4\)H\(_10\)) 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. Tedlar bags of polypropylene (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).

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):

\[
R_s = \frac{2 \times (t_{rA} - t_{rB})}{wA + wB}
\]

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).

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 according as 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 °C). 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):

\[
\text{Recovery} = \frac{C_1}{C_2} \times 100
\]

where \(C_1\): experimental concentration of analyte in the fortified sample; \(C_2\): 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: \(H_2/O_2\), \(N_2/CO\), \(CO/CO_2\), \(CH_4/C_2H_2\), \(C_2H_4/C_2H_2\), \(C_2H_6/C_2H_4\) (propyne), \(C_3H_6/iso-C_3H_8\) and \(iso-C_3H_8/n-C_3H_8\), thus indicating a separation of 100% between the peaks of each of these analytes. \(R_s\) 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. 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                          | linear velocity    |
| Flow control mode                              | 16 kPa (10 min), rates of 12, 24, 48 and 60 °C min⁻¹ up to 240 °C |                    |
| Pressure / kPa                                  |                                                      |                    |

TCD: thermal conductivity detector; FID: flame ionization detector; He: helium; Ar: argon.
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$_3$H$_4$ (propyne and propadiene), C$_3$H$_6$ and C$_4$H$_{10}$ (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.

### Table 3. Rs 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 | Rs  |
|------------------|-----|
| 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$_2$H$_4$| 8.42|
| C$_2$H$_4$/C$_2$H$_6$ | 2.97 |
| C$_2$H$_4$/C$_2$H$_6$ | 1.90 |
| C$_2$H$_4$/C$_2$H$_4$ | 8.66 |
| C$_3$H$_4$/C$_3$H$_4$ | 1.38 |
| C$_3$H$_6$/C$_3$H$_6$ | 1.26 |
| C$_3$H$_6$/C$_2$H$_4$ | 1.37 |
| C$_3$H$_6$/iso-C$_4$H$_10$ | 7.24 |
| iso-C$_4$H$_10$/n-C$_4$H$_10$ | 1.92 |

*Propadiene; †propyne. Rs: resolution.

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$_2$H$_6$ (8.0 ± 0.5) > C$_3$H$_6$ (6.2 ± 0.1) > C$_3$H$_8$ (5.9 ± 0.2) > C$_2$H$_4$ (2.8 ± 0.3) > n-C$_4$H$_10$ (2.7 ± 0.3) > N$_2$ (5.8 ± 0.2) > iso-C$_4$H$_10$ (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 (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$^{-3}$) (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

Figure 1. (a) TCD chromatograms and (b) FID obtained from the mixture of inorganic gases and light hydrocarbons under the best chromatographic conditions.
A Gas Chromatography Method for Simultaneous Quantification of Inorganic Gases and Light Hydrocarbons

J. Braz. Chem. Soc.

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
(∑C1-C4 = 52.1% v/v) and absence of H2 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.

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

| Analyte | Evaluated range / ppm | Linear range / ppm | Linearity (r) | LODa / ppm | LODb / ppm | LOCd / ppm |
|---------|-----------------------|--------------------|--------------|------------|------------|------------|
| H2      | 2.75 to 210           | 8.96 to 210        | 0.99309      | 2.75       | 5          | 0.6        | 8.96       |
| N2      | 0.0916 to 101         | 0.314 to 101       | 0.99995      | 0.0916     | 50         | 11.2       | 0.314      |
| O2      | 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       |
| CO2     | 0.732 to 270          | 2.46 to 270        | 0.96979      | 0.732      | 25         | 0.1        | 2.46       |
| CH4     | 0.0916 to 274         | 0.314 to 274       | 0.99811      | 0.0916     | 1          | 0.06       | 0.314      |
| C2H6    | 0.0916 to 210         | 0.314 to 210       | 0.99962      | 0.0916     | 1          | 0.05       | 0.314      |
| C2H4    | 0.0916 to 224         | 0.314 to 224       | 0.99964      | 0.0916     | 1          | 0.04       | 0.314      |
| C3H6    | 0.0916 to 224         | 0.314 to 224       | 0.99960      | 0.0916     | 1          | 0.04       | 0.314      |
| C3H4e   | 0.0916 to 193         | 0.314 to 193       | 0.99978      | 0.0916     | –          | –          | 0.314      |
| C3H4f   | 0.0916 to 193         | 0.314 to 193       | 0.99962      | 0.0916     | –          | –          | 0.314      |
| C3H8    | 0.0916 to 210         | 0.314 to 210       | 0.99943      | 0.0916     | –          | –          | 0.314      |
| C4H8    | 0.0916 to 210         | 0.314 to 210       | 0.99919      | 0.0916     | –          | 0.2        | 0.314      |
| iso-C4H10 | 1.83 to 193          | 6.05 to 193        | 0.99511      | 1.83       | –          | –          | 6.05       |
| n-C4H10 | 3.67 to 224           | 12.1 to 224        | 0.99889      | 3.67       | –          | –          | 12.1       |

aLOD of the present work; bLOD of the ASTM D3612-02 (method A); cLOD of the ASTM D3612-02 (method C); dLOQ of present work; epropadiene; fpropyne.

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.

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
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.
Acknowledgments

The authors thank FAPEMIG for the scholarship to Valdislaine M. Silva. The authors are also grateful for the financial support provided by Furnas Centrais Elétricas S.A., Carbogás Energia Ltda., Agência Nacional de Energia Elétrica, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) (001), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). Alam G. Trovó is grateful to CNPq (grant 405043/2018-0 and research fellowship 305215/2018-3) and Fundação de Amparo à Pesquisa do Estado de Minas Gerais FAPEMIG (grant PPM-00509-18).

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; Solidônia 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, methodology, investigation, visualization, supervision, project administration and funding acquisition.

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Submitted: November 10, 2020
Published online: January 27, 2021