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Ega-Py/Gc/Ms Study of the Compounds Generated in the Decomposition of Hnb Heet and Neo Tobaccos Under Inert and Oxidative Atmospheres; Comparison with 3r4f Tobacco

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Abstract

Compounds generated when heating two HNB tobaccos (Heet and Neo) and a conventional tobacco (3R4F) were studied by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The Py-GC/MS experiments were carried out in He and air atmosphere at 250, 300, 350 and 400 ºC. HNB systems use a type of reconstituted tobacco that each brand produces for adapting to their corresponding devices. The results show that these types of tobaccos generate larger amounts of nicotine and glycerol than conventional tobacco. Moreover, compounds as phenol (under inert and oxidative atmosphere), acetaldehyde, acetone, formaldehyde and phenol (under oxidative atmosphere) classified in FDA's HPHC list are generated at these temperatures (i.e.: 250-400 ºC). Therefore, it can be concluded that although initially HNB tobaccos are less harmful to health than conventional cigarettes, they are not exempt of risk.

Keywords: EGA-Py/GC/MS; HNB; Tobacco; Nicotine

Introduction

Conventional cigarette smoke presents more than 8000 different compounds [1], resulting from the distillation and evaporation of tobacco components as well as from the combustion, pyrolysis and pyrosynthesis processes that take place during smoking. Temperatures up to 900 ºC are typically reached in these processes. At least 250 of such compounds are known to be harmful, including hydrogen cyanide, carbon monoxide, and ammonia and 69 compounds have confirmed carcinogenic activity in humans [2, 3]. These compounds include the tobacco-specific nitrosamines (TSNA) that are found in the tobacco leaf and are transferred to the smoke by evaporation at low temperatures (around 150 ºC for the most volatile). Also, the polycyclic aromatic hydrocarbons (PAH) also present a very high toxicity and are formed at temperatures above 800 ºC. Short-chain aldehydes such as formaldehyde, acetaldehyde, acrolein, which are formed by pyrolysis of the carbohydrates in the leaf at temperatures between 150 and 300 ºC are also among those very harmful compounds present in the tobacco smoke.

The pressure of public opinion has forced tobacco companies to try to reduce the toxicity of smoking articles and thus improve their image in society. In this line, during the first decade of 2000, cigarettes with a reduced tar / nicotine (T / N) ratio were developed [4] and recently they have developed a new generation of "Heat but Not Burn" (HNB) cigarettes. This was an older approach that had no commercial successful in the past. In these products, the tobacco, which is formed by a type of reconstituted tobacco, is heated to temperatures between 200 and 350 ºC, much lower than the 900 ºC found in conventional cigarettes. This prevents combustion reactions from occurring, where most of the CO is generated, and enough heat is generated to maintain the pyrolysis and pyrosynthesis reactions at elevated temperatures in conventional cigarette smoking. In HNB cigarettes, the aerosol inhaled by smokers comes from the evaporation of volatiles and the pyrolysis of tobacco components at low temperatures. According to tobacco companies, nicotine and total particulate matter are kept in these cigarettes at values close to those of conventional cigarettes, but toxic compounds show reductions between 70 and 95%, depending on the electronic device used and the type of tobacco smoked. For this reason, these products have been promoted as a novel, technological, clean and pure product, a very attractive communication strategy for adolescents and young people [5].

However, according to a study carried out by the Spanish Society of Pulmonology and Thoracic Surgery (SEPAR) on electronic cigarettes and IQOS [6], adolescent users of some of these tobaccos have urinary cotinine levels that almost double those found in conventional cigarette smokers, confirming initial fears that these devices promote nicotine addiction. Authors such Chaiton and Schwartz [7] pointed out the necessity of carrying out independent studies to support the lower toxicity of these cigarettes. According to these authors, in the first generation of HNB commercialized in the 90s, the tobacco industry claimed that the smoke was free of toxic compounds, but several independent studies showed years later that, comparing them with conventional cigarettes, higher yields of some toxic compounds were obtained, among them carbon monoxide and formaldehyde [8].

In recent years, interest in HNB cigarettes has grown, which has resulted in an increase in publications on this topic. These works range from the study of the impact of this tobacco on the consumption of the society [9-11], different designs of devices for this type of cigarettes [12, 13] to the study of different compounds produced in smoke when smoking at low temperatures. Various authors study nicotine levels and emissions in HNB [14-16] or the (HPTC) harmful and potentially harmful constituents in mainstream emissions [17-19] or the particulate matter and HPHC in secondhand emissions [20-22]. Under the ISO regimen, Auer et al. find that the regular IQOS tobacco was yielded 0.30 mg of nicotine [14] while under the HCI regimen [15, 16, 17-19] the nicotine levels in mainstream aerosol were 1.10–1.41 mg for IQOS. Nevertheless, we have found no studies of the effect of potential catalysts for reducing the generation of toxic compounds when smoking these types of tobaccos.

Thermogravimetric analysis (TGA) is a technique commonly used for monitor the different processes of mass loss that occur in thermal degradation of many materials [23–25], but it does not allow distinguishing the compounds generated. Pyrolysis gas chromatography mass spectrometry (Py-GCMS) is a powerful technique that can be used to characterize most materials including insoluble and complex materials at trace levels often without any sample pretreatment. The EGA/PY permits pyrolyzing different types of samples under different atmospheres and heating regimes. The direct gas introduction in a GC/MS allows the separation of the compounds generated for their identification, thus providing valuable information of the thermal decomposition behavior of the samples including the product distribution and its evolution with temperature complementing the information provided by TG.

In previous papers we have studied by this technique the behaviour of the 3R4F tobacco under inert and oxidative atmospheres at high temperatures, as well as the effect of different catalysts at high temperatures [26, 27].

This article is the first of a series with the objective of studying the thermal decomposition behaviour of HNB tobaccos and the effect of the catalysts used in conventional cigarettes in the temperature ranges typical of the devices used for smoking these types of tobaccos. In this work we present and discuss the results obtained in the pyrolysis of two HNB tobaccos (Heet and Neo) under inert and oxidative atmospheres at temperatures between 200 and 400 ºC, and compared with those obtained with the 3R4F reference tobacco under the same conditions. These results will be the reference for studying the effect of the different catalysts used.

Materials and Methods

Two brands of HNB cigarettes marketed in Spain have been selected for this study. The first one was Heet tobacco amber selection, and the second was Neo classic tobacco. Both are characterized by presenting a flavour similar to conventional tobacco within the wide range marketed by both brands, and were acquired in a tobacco shop in the area. Heet tobaccos are tobacco products created by Philip Morris International exclusively designed for use with a precisely controlled heating device that they market under the brand name IQOS. NEO tobacco is a similar product manufactured by British American Tobacco (BAT) developed for its controlled heating systems known as Glo. Reference tobacco 3R4F was supplied by University of Kentucky, and was used as an example of conventional tobacco, and its composition include Flue-cured 35.41%, Burley 21.62%, Maryland 1.35%, Oriental 12.07%, Reconstituted (Schweitzer process) 29.55%, Glycerol (dry-mass basis @ 11.6% OV) 2.67%, Isosweet (sugar) 6.41% [28].

The decomposition of the different samples were analysed in a thermobalance Metller Toledo TGA/DSC1 under inert and oxidative atmospheres (N_2 and Air). Experiments were carried out under dynamic conditions were the sample was heated from 30 to 700 °C at 35 °C min^{-1} under a flow of 80 mL min^{-1} (STP).

The compounds generated during the decomposition of the samples were analysed in a multi-shot pyrolyser (EGA/Py-3030D, Frontier Laborato-ries Ltd.), which was attached directly to a GC/MS (6890 N GC/5973 inert MSD, Agilent technologies). The different compounds generated at the different temperatures studied were introduced into the GC separation capillary column and analysed by MS. About 400 µg of the tobacco were heated at the temperature studied during 1 min, under inert atmosphere of helium, and oxidative atmosphere of air. The reaction products were introduced into the GC separation column (HP-5MS UI, 30 m×0.25 mm i.d.×0.25 µm film thickness, Agilent Technologies) with a split ratio of 50:1 (column flow rate: 2 mL min−1) using helium as carrier gas. The separated compounds were detected by MS (the temperature of the GC/MS transfer line was 280 °C and the MS source and MS Quad temperature were 230 and 150 °C, respectively). The mass spectrometer was operated in electron-impact mode at 70 eV at scan range of 15–350 amu. The compounds were identified by the NIST 08 library (National Institute of Standards and Technology, USA) and/or Wiley7n library (Wiley Registry of Mass Spectral Data, 7th Edition).

Results and Discussion

Figure 1 shows a picture of the different tobaccos types. As can be seen, tobacco 3R4F is made up of strands of different lengths from different varieties of tobacco (Figure 1a). Heet tobacco (Figure 1b) is made up of a very homogeneous tobacco (color, length) made up of small sheets bundled together. Finally, Neo tobacco (Figure 1c) has strands of similar length and appears to be made up of reconstituted tobacco giving rise to samples more similar to conventional tobaccos.

Thermogravimetric Analysis

A prelaminar thermogravimetric study in a thermobalance was done. Figure 2a shows the derivative thermogravimetric curves (DTG) obtained for reference tobacco 3R4F, Heet and Neo tobacco under inert atmosphere, normalized by the tobacco mass. All tobaccos present the same decomposition steps: evaporation of moisture at temperatures lower than 125ºC, with DTG peak temperature at around 80 ºC; evaporation of glycerol and other volatile compounds in the range 120-250 ºC; two overlapped processes in the range 230-375 ºC corresponding to decomposition of hemicellulose and cellulose respectively; pyrolysis of lignin occur in a wide range of temperature at around 450 ºC; dehydrogenation and aromatization of char and/or decomposition of endogenous inorganic compounds at around 650 ºC. Moreover, the proportion of the different decomposition steps changes, being the more remarkable the great increase in the peak associated with the elimination of glycerol at 205 ºC. This is in accordance with the manufacturers that indicate that HNB tobaccos present a mixture of 70% tobacco and 30% glycerol [29] while 3R4F tobacco has a glycerol content of 2.67% [28].

It can also be observed that the three samples present similar peaks associated with the decomposition of hemicellulose and cellulose. Nevertheless, HNB tobaccos present a lower contribution of the first peak associated the hemicellulose. Neo tobacco shows a larger contribution of the cellulose peak. Moreover, the temperature of decomposition of cellulose is slightly higher for HNB with respected to 3R4F (335 ºC vs 325 ºC). The contribution of the process taking place at temperatures higher than 350 ºC (probably associated to lignin) is larger foe 3R4F tobacco, as well as the last peak at temperatures higher than 625 ºC and probably associated to the decomposition of inorganic matter.

The behavior of the different tobaccos in an oxidizing atmosphere is shown in Figure 2b. As can be seen, until the decomposition of hemicellulose (275 ºC) the DTG curve shows a behavior identical to that observed in an inert atmosphere. But at higher temperatures, the cellulose decomposition peak is affected by the oxidizing atmosphere and an important and sharp peak is observed over 425 ºC associated with the combustion of tobacco. However, HNB devices are heated up to a maximum of 400 ºC, ensuring that they do not reach the combustion temperature of tobacco. Heet tobacco undergoes a larger amount of reactions at temperatures below 350 ºC, thus producing larger amount of volatiles within the normal smoking temperatures for this type of tobaccos.

Analysis of the products of decomposition of HNB: inert and oxidative atmosphere

Py-GC/MS analysis was carried out to identify and semi quantify the products obtained. In order to avoid the influence of the mass of sample, the peak area was normalised by dividing it by the initial mass of tobacco analysed. Experiments were replicated three times and showed that the reproducibility of the results (i.e. the peak area/amount of tobacco loaded) is better than 10% for all compounds detected. The mean values of the three experiments are shown in the tables in the supplementary material (Tables A1-A6).

Figure 3a shows the three principal compounds obtained by Py-GC/MS in the pyrolysis of three tobaccos studied under inert atmosphere of Helium, Nicotine, Glycerol and CO_2+H_2O. The range of temperatures studied was from 250 to 400 ºC in steps of 50ºC. These temperatures studied were selected to cover the range of working temperatures of the HNB devices available on the market in Spain, that work between 260 ºC for the Glo device (Neo tobacco) to 400 ºC for the IQOS device (Heet tobacco). CO_2 and water were grouped in the same peak due to the difficulty of resolving/separating both compounds peaks.

As can be seen, all tobaccos present the same behaviour with respect to the CO_2+H_2O peak, with similar values at the same temperature and when the temperature increases, the peaks of CO_2+H_2O increase, showing the increased tobacco decomposition. Carbon dioxide and water was mainly caused by the decomposition and reforming of carboxyl, carbonyl and carboxylic acid functional groups of hemicelluloses and cellulose [30].

Glycerol is added to tobacco mainly as a softening and moisturizer additive. As can be seen, Heet and Neo tobaccos present much more glycerol than the conventional tobacco 3R4F as indicated by the manufacturers [28, 29], being Heet tobacco the one with the highest amount of glycerol. The nicotine is produced by distillation, and is always accompanied by some degradation of the tobacco [31]. Heet and Neo tobacco show similar values of Nicotine, these being much higher than those observed for 3R4F tobacco at any temperature, the major increase in its production is observed at 400 ºC. The amounts of Nicotine, in the case of the 3R4F tobacco, are similar to those of glycerol, whereas in the cases of Heet and Neo tobaccos the peak of glycerol is, by far, the most abundant. Summarizing, it can be concluded that all the three tobaccos present a similar behaviour with respect to CO_2+H_2O, thus having similar composition of hemicellulose and cellulose, but both HNB tobaccos have been loaded with significant amounts of nicotine and mainly glycerol. These results are in good accordance with those obtained in DTG curves, where Heet is the tobacco showing a larger peak corresponding to glycerol.

Figure 3b shows the evolution on CO_2+H_2O, Glycerol and Nicotine obtained for the tobaccos HNB and 3R4F under the oxidative atmosphere of Air obtained by Py-GC/MS. As can be seen all these compounds were generated in larger proportion in oxidative atmosphere than inert one and again the proportion of glycerol obtained from HNB tobaccos are similar and larger than that obtained for the 3R4F reference tobacco. Concerning nicotine, although it is again formed in greater quantities in the case of the decomposition of HNB tobaccos, the values obtained in the decomposition of 3R4F are only slightly lower. It may be that the nicotine added to both HNB tobaccos is more reactive under oxidizing conditions than that in the 3R4F tobacco.

CO_2+H_2O peak presents again a similar behaviour for the three tobaccos and the same evolution with temperature as that observed under inert atmosphere. Nevertheless, the behaviour observed for glycerol and nicotine when increasing temperature is the opposite to that observed under inert atmosphere, since now these compounds decrease when increasing temperature, for all the three tobaccos. These results are in good accordance with the work of Calabuig et al. [27], where the authors studied the decomposition of 3R4F at 300, 500 and 700 ºC under similar atmospheres, both inert and oxidative. Calabuig et al. results showed that nicotine and glycerol where produced in larger proportion under oxidative atmosphere than under inert atmosphere. In addition, when the temperature exceeded 500 ºC, nicotine production decreases, slightly under inert atmosphere and quickly under oxidative atmosphere, almost disappearing at the zone of combustion temperature (700 ºC). Nicotine has a boiling point of 247 ºC, and it is obtained by distillation at the work temperatures of the HNB devices (250-400ºC) and at higher temperatures the quantity obtained decreases because it begins to decompose. Similar results were obtained by Asensio [32] that studied the decomposition of pure nicotine under inert and oxidative atmosphere. He found that under inert atmosphere nicotine does not practically decompose, only distils, but under an oxidizing atmosphere at low temperatures, around 300 ºC, it begins to decompose generating compounds like myosmine and nicotyrine. In summary, Figures 3a and 3b show that HNB tobaccos have a higher amount of nicotine and glycerol than conventional tobacco and that they are easily released under the normal smoking conditions of HNB tobaccos. Also, it can be concluded that oxidizing atmospheres promotes the evolution of all compounds under the conditions in the EGA equipment, mainly glycerol and that glycerol and nicotine undergo increasing decomposition reactions when increasing temperature.

Figures 4 show the rest of the compounds detected by Py-GC/MS in the decomposition of Neo, Heet and 3R4F tobaccos at the different temperatures under inert atmosphere. These compounds are presented grouped by functional groups, where glycerol was not included in the alcohol family, and nicotine was not included in the nitrogenated one. All compounds detected but not identified were grouped in the Not Assigned family. As can be seen in Figure 4 for 3R4F and Heet tobacco, acid compounds and carbonyls are the most abundant families, but in the case of Neo aliphatic compounds are also generated in a high proportion, as high as those of acid compounds and carbonyls. In general, for all the families and tobaccos brands, all compounds increase when the temperature increases. Calabuig et al. [27] in their Py-GC / MS study of the decomposition of 3R4F, observed an increase in the formation of all chemical families between 300 and 500 ºC, but at higher temperatures, 700 ºC, they observed a decrease in the formation of the chemical families and only maintain this tendency the aromatic, aliphatic and unassigned compounds, that show a major formation. The two HNB tobaccos present similar amounts of all families of compounds and more quantity of acid, carbonyl and aliphatic compounds than 3R4F. Nevertheless, Neo is the tobacco presenting larger amount of aliphatic compounds. This is agreement with the results observed in the DTG curves (Figure 2a) where a greater increase was observed for HNB tobacco in the peak of volatiles and glycerol, as well as the larger peak in the decomposition of cellulose for Neo tobacco.

The more abundant compound within every family group appears in Figure 5. Acid acetic is the major compound in the acid family and is due to the decomposition of hemicellulose that is rich in acetyl group [33]. With the carbonyls compounds, 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-Pyran-4-one, is the major compound at all the temperatures and is due to the pyrolysis of 1-deoxy-l-(l-prolino)-d-fructose and another sugar-amino acid compounds [31]. Cotinine is an alkaloid derived from the decomposition of nicotine. Furfural is a natural aroma component in tobacco and is also present in cigarette smoke [34]. Hydroquinone is a product of the thermal decomposition of compounds present in tobacco and has a boiling point of 287 ºC somewhat higher than that of nicotine. As can be seen, most of these compounds were generated in major proportion when the temperature increases, being acid acetic the more abundant. Cotinine shows a maximum at 300 ºC for Heet tobacco, at 350 ºC for Neo tobacco and 3R4F presents the larger production at 400 ºC. Eicosane increases with temperature for the here tobaccos and presents the larger values for Neo tobacco. With respected to 3R4F, in the work of Calabuig et al. [27] a similar trend is observed where the amount of these compounds increases between 300 and 500 ºC, but at temperatures close to combustion, their formation decreases as they decompose into other products, generally obtaining amounts lower than those obtained at 300 ºC.

The decomposition of the tobaccos by Py-GC/MS under oxidative atmosphere (Figure 6) grouped by chemical families shows similar tendency to that obtained under inert atmosphere (Figure 4), presenting an increase in the all the families of compounds when increasing temperature. As observed in the case of nicotine and glycerol (Figure 3), it is worth noting that a greater amount of compounds are generated under oxidizing atmosphere, about three times more compounds, than under inert atmosphere. Again, acid and carbonyls compounds are the most abundant families. Within these two families it is observed that at low temperatures (250-300ºC) Heet tobacco is the one that generates the largest amounts, while at higher temperatures (350-400 ºC) it is Neo tobacco that produces more compounds. In general, it is observed that for all families, and at all temperatures, HNB tobaccos generate more compounds than the 3R4F tobacco, with the exception of nitrogenated family that are formed in a higher proportion for 3R4F at 400 ºC. At high temperatures, 700 ºC, when the combustion of conventional tobacco occurs, Calabuig et al. [27] observed, as in the case of pyrolysis, that the compounds generated in the decomposition of 3R4F, decrease, except for aromatics, aliphatics and the family of not assigned compounds, being not assigned the chemical family that increases the most.

Despite the similarity of Figures 4 and 6, the distribution of products changes significantly. Thus, for example, within the carbonyls compounds the most abundant compounds in oxidative atmosphere are acetone, acetaldehyde and 2,3-Butanedione. In general, these compounds could be generated by the degradation of glycerol and sugars present in tobacco [35]. 3-methyl-1-phenyl-1H-Pyrazole and 2,3'-Dipyridyl are the most abundant nitrogenated compounds and are alkaloids generated as a result of the decomposition of nicotine [32, 36]. Within aromatics compounds, hydroquinone is one of the most abundant, as in inert atmosphere but it is surpassed by the formation of phenol that was produced to a lesser extent under inert atmosphere. Both compounds are produced by the thermal decomposition of compounds present in tobacco such as chlorogenic acid [37, 38]. Furfural is a fragrance used as flavour in heated tobacco products. These main compounds of the different families are represented in Figure 7 vs temperature.

It should be noted that several of the most abundant compounds such as acetaldehyde and acetone in the family of carbonyls and phenol in aromatics are included in the FDA's HPHC list. Acetone is considered as a respiratory toxicant. Acetaldehyde, the second in abundance among carbonyls, is considered carcinogen, respiratory toxicant and addictive, and is listed by the international agent for Research on Cancer (IARC) within group 2B (possible carcinogenic to humans). Phenol is respiratory toxicant and cardiovascular toxicant and in classified in the group 3 (Not classifiable as to its carcinogenicity to humans). And it must be not forgotten that nicotine, despite not being classified in any group by the IARC, is considered reproductive or developmental toxicant and addictive.

As can be seen, acetic acid, furfural and eicosane were detected in both atmospheres. The proportion of eicosane obtained for 3R4F and Heet tobaccos is higher under oxidative atmosphere. Acid acetic increases slightly for 3R4F and Heet, whereas presents the largest values and increase with temperature for Neo tobacco (Figure 7). Furfural shows and important increase in its formation for all the tobaccos with temperature, and shows a similar tendency than under inert atmosphere. The main compound in the carbonyl family was acetone, and in second place acetaldehyde. Both compounds appear in Figure 7. Acetaldehyde has been added due to its high toxicity. Acetone and acetaldehyde shown similar tendency, and increase in their formation when the temperature increases, for 3R4F and Heet tobacco, but for Neo tobacco seems that a maximum quantity is obtained at 350 ºC, and at 400 ºC its production decreases slightly. It should also be mentioned that the amount of these products generated is significant, accounting for about 40% of the carbonyls. On another hand, phenol production increases when the temperature increases, showing similar behaviour for all tobaccos to that observed for acetaldehyde, but with lower yield. Calabuig et al. [27] observed that the amount obtained of acetaldehyde, acetone, and phenol, increases between 300-500 ºC and decreases at higher temperatures, 700 ºC, when studying the for 3R4F tobacco. Compounds such as acetone were not formed at such high temperatures. It should also be mentioned that despite decreasing the amount obtained of these compounds, a greater quantity of them is obtained at 300 ºC than at 700 ºC.

Conclusions

HNB cigars are marketed with the widespread idea that they are much less harmful than conventional tobacco because when heated to their working temperatures, well below the ignition temperature, much of the common toxic of tobacco smoke are not produced. In addition, HNB systems do not use natural tobacco, the corresponding cigarettes being made with a type of reconstituted tobacco that each brand produces for adapting to their corresponding devices.

Based on the data obtained, it can be concluded that the HNB tobaccos studied include much larger amounts of nicotine and glycerol than the 3R4F tobacco. Despite the very well-known fact that this type of HNB systems and tobaccos generate much less quantity of toxic compounds as compared to conventional smoking, due to the lower temperatures used they deliver larger amounts of nicotine and glycerol than conventional smoking, and this is true also at the low temperatures of these systems, since both HNB tobaccos deliver under EGA conditions tested larger amounts of nicotine and glycerol than the 3R4F reference tobacco, what, a priori, could trigger a greater addiction to this type of tobacco, increasingly popular among young people.

Moreover, chemical compounds classified in FDA's HPHC list are generated at low temperatures (250-400 ºC). Among these compounds, phenol has been detected under inert atmosphere in low concentration. But, under oxidizing atmosphere, significant quantities of various compounds on the list have been obtained, such as acetaldehyde, acetone, formaldehyde and phenol. Therefore, we can say that although initially they are less harmful to health than conventional smoking, they seem to be not innocuous.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit authorship contribution statement

Deseada Berenguer: Visualization, Methodology, Investigation, Validation, Data curation, Writing- Original draft preparation.
Antonio Marcilla: Conceptualization, Methodology, Supervision, Writing- Reviewing and Editing, project administration.
Isabel Martinez: Resources and Methodology.

Supplementary

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