NEW TOOL FOR DEVELOPING LOW-EMISSION INKJET INKS

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ABSTRACT

The ceramic industry has evolved in recent years towards digital technology in its decorating systems, which has led, as was expected, to improved quality of the end product. This adaptation to the digital world has entailed the use of organic compounds totally different from those traditionally used to formulate ceramic inks. In addition, the trend in digital decorating calls for increased ink laydowns, which has thus aroused even further - should that be possible - the industry's concern about these new products' environmental performance.

Due to the large number of variables that influence the generation of emissions during the ceramic firing process, it is difficult at laboratory level to reproduce the conditions that occur in kilns in order to estimate the potentially hazardous products that are likely to be exhausted through the chimney stack.

The aim of this study is to present analytical pyrolysis as a work tool that enables scientific comparison to be performed, with emphasis on the intrinsic characteristics of the various products, the emissions generated within reproducible conditions that have been amply contrasted by the use of this technique in other industries, and thus to explain how it can help in the reliable formulation of safer products.

Although the conditions in analytical pyrolysis do not reproduce the actual atmosphere of a ceramic kiln, the multitude of variables that directly influence the conditions occurring in the combustion chamber when a worst-case scenario is simulated (absence of oxygen) show analytical pyrolysis to be a useful and demanding tool for comparing the emissions generated by different products.

Our work has enabled us to compare a large number and variety of organic products compatible with inkjet technology, and so to choose the best alternatives for developing compositions that perform better and beyond current legal limits in regard to the generation of potentially hazardous products.

The results obtained need to be confirmed under industrial conditions that are impossible to reproduce in the laboratory. The emissions generated for the same product may vary depending on the specific conditions at each industrial site.

1. INTRODUCTION

Throughout history, the ceramic tile manufacturing process has undergone several vital technological revolutions that, at the time, represented both a technological and economic breakthrough and without which, ceramics could not be understood the way it is conceived today. One such technological revolution was the arrival in the industry of inkjet decoration. Since the year 2000, when the first digital printing machine made its appearance, the inclusion of this type of decorating system in the ceramic sector has been practically universal.

Inkjet decoration brought a significant reduction in material laydown per square metre compared to previous decorating systems (flat screen printing, rotogravure, ...), and remarkable colour intensity was achieved using a mere 10 g of ink per square metre. Today, with the quest for new effects and the development of new printing heads with greater jetting capabilities, laydown levels of up to 100 g per square metre of inkjet ink are being achieved.

In the face of such jetting levels and the fact that about 50-70% of the ink composition comes from the different organic compounds included in the formulation to produce stable inks, the emissions of compounds generated by combustion during the firing process have become a greater concern for the sector.

The regulations set down by Royal Decree 515/2013, which approves the Industrial Emissions Regulation in implementation of Law 16/2002 on Integrated Pollution Prevention and Control, are confined to certain compounds and only to those that are exhausted through the chimney stack as a product of actual combustion, which is why understanding those exhausted products is vital to developing environmentally sustainable products.

The ceramic industry's concern for the environment has led to a study of decomposition products under industrial conditions and through simulation of those conditions in the laboratory, and to the introduction of improvements in inkjet product formulations to minimise emissions of potentially hazardous substances. Those studies generally refer to very specific experimental conditions in which a large number of variables intervene, which is why they are so difficult to reproduce. Some of the most prominent variables are the different conditions occurring in industrial kilns, interactions with different types of ceramic substrates, and the complexity of ink formulations.

As a result, all these initiatives are seriously limited in that, so far, it has not been possible to accurately study under controlled atmospheric conditions the reaction products generated. Nor has a fast, reliable and reproducible method been defined that would enable the outcome of formulation improvements in different usage conditions around the world to be predicted.

As is well known, the thermal cycle in a ceramic kiln (Mezquita *et al.*, 2014) consists of various stages (Fig. 3).

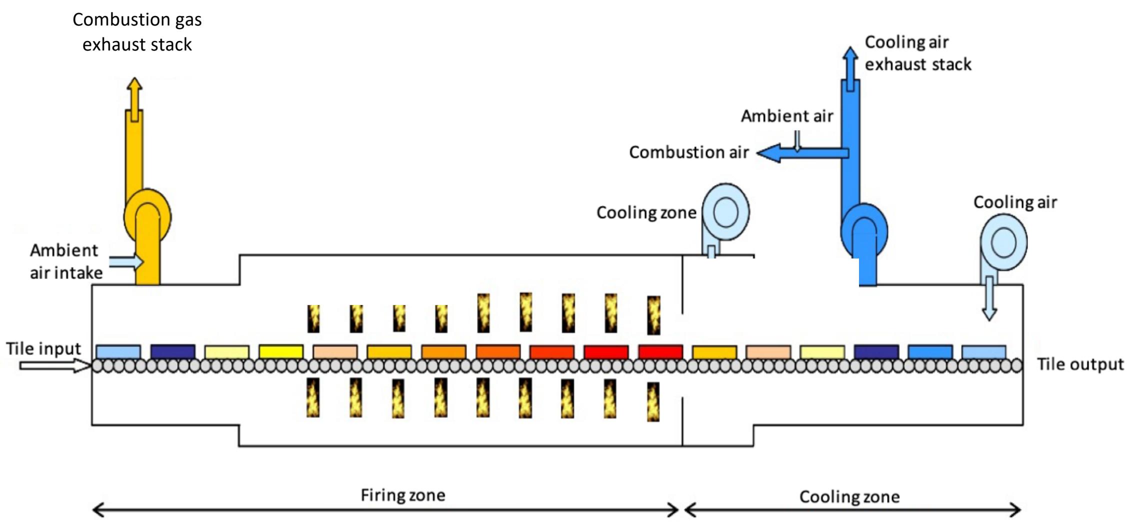


Fig. 3. *Diagram of a ceramic kiln*

In the case at hand, the area of study focuses on the stage between 400ºC and 900ºC, which is where the majority of organic reactions take place.

Detailed studies of the ceramic cycle (Mezquita *et al.*, 2014) were able to verify that the oxygen level in our analytical pyrolysis study area (i.e., 400ºC - 900ºC - the range where organic substances decompose), is well below the usual 21% in the atmosphere, with values clearly below 10% (Fig. 4).

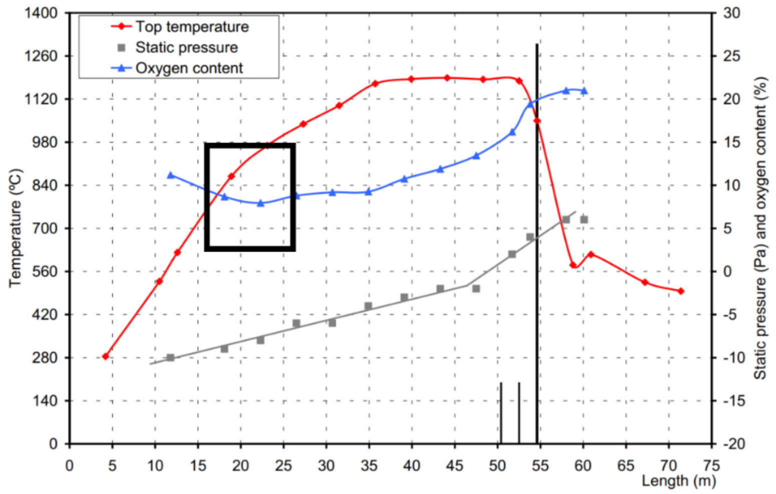


Fig. 4. *Static pressure and oxygen content readings inside a ceramic kiln*

This, together with the fact that at microscopic level, the outer layers of material keep the reaction zones devoid of oxygen, makes a study of the compounds generated in an atmosphere void of oxygen, i.e., in the worst-case scenario, more plausible.

This paper proposes analytical pyrolysis as a tool for comparing the compounds generated in extreme conditions, which, together with other techniques already used in the sector, will help to determine which products or formulations are the best candidates for reducing the emissions generated in the ceramic process. As stated, our test conditions take place in the absence of oxygen, which is why it represents the worst-case scenario that can be encountered.

The analytical pyrolysis technique involves coupling a pyrolizer with gas chromatography and mass spectrometry: Py-GC/MS. It is a high-resolution tool that has proven to be very useful for direct characterisation (with no prior manipulation) of natural and synthetic pigments and their additives, solvents or binding bases, not only in ready-made paint and varnish samples but also in low concentrations embedded in diverse and complex matrices (Ghelardi *et al.*, 2015; Russell *et al.*, 2011; Sonoda, 1999).

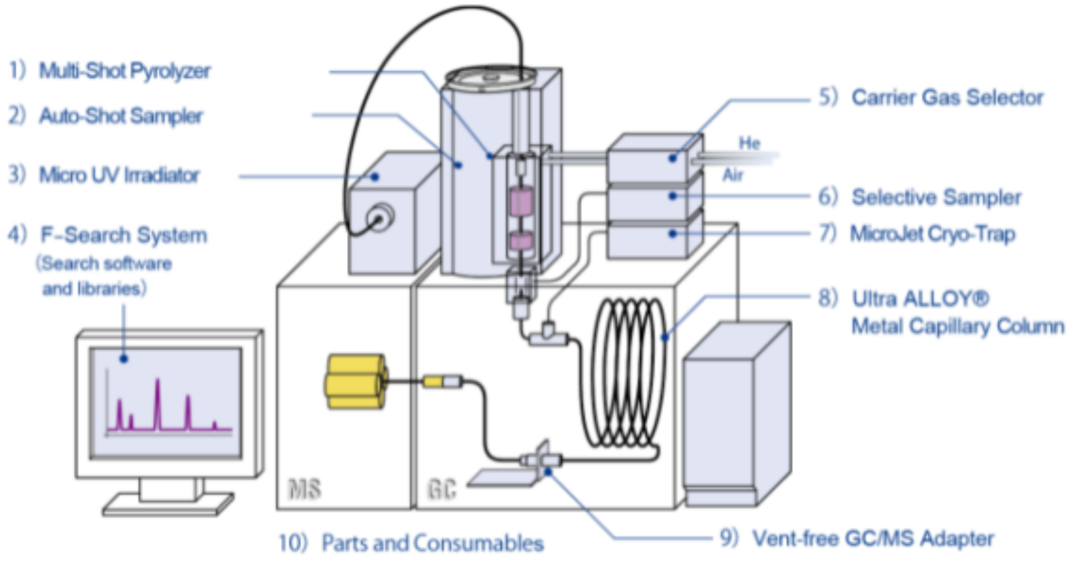


Fig. 1. *Analytical pyrolysis system (Py-GC / MS) (www.grupo biomaster.com)*

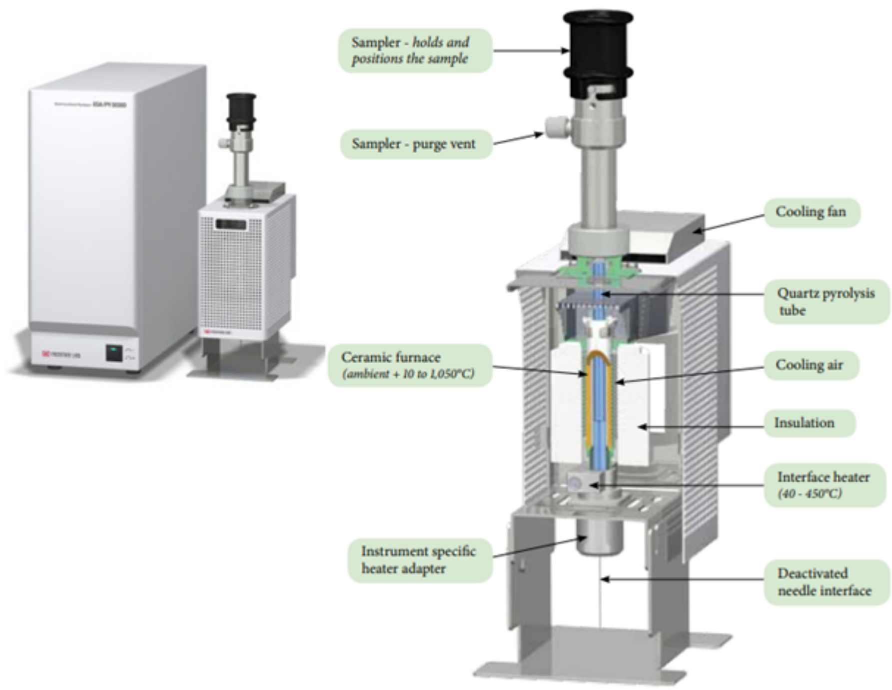


Fig. 2. *A pyrolyzer and its component parts (www.grupo biomaster.com)*

Analytical pyrolysis has also been used to evaluate the toxicological properties of pigments such as those used in tattooing (Schreiver *et al.*, 2016) and in printed paper (Wei *et al.*, 2016). In addition, Py-GC/MS can be used to reproduce pyrolysis conditions (Lu *et al.*, 2011) and the fragments detected by this technique can be studied to evaluate decomposition products present in toxic fumes and vapours that may be potentially hazardous for human health (Chetehouna *et al.*, 2018; de Sa *et al.*, 2017; Wei *et al.*, 2016; Jones *et al.*, 2005) and which may be generated, for example, during the firing of ceramic materials.

In this sense, when analytical pyrolysis is carried out under constant and reproducible test conditions, the technique is useful for identifying the intrinsic properties of tested materials and the differences in emissions that may occur at high temperatures.

Consequently, in order to study the role played by various substances used in inkjet inks in generating potentially hazardous products, standard test conditions were established which, although they can never fully represent the conditions of an industrial kiln, are useful when comparing the emission behaviour of the various products under study.

2. METHOD

For the tests carried out in this study, an analytical pyrolysis unit (Py-GC/MS) was used, consisting of a micro-furnace pyrolyzer (Frontier Labs, Fukushima, Japan, model 2020iD) coupled to a gas chromatograph (Agilent, model 6890N) with a low-polarity capillary column (Hp 5MS-UI; 30m x 250µm x 0.25µm). The analyser used was a selective mass spectrometer (Agilent, 5973 MSD) and the mass spectra were obtained at a specific fixed voltage for all the tests (Fig. 1).

The instrument allows for precise selection of thermal desorption or pyrolysis temperature between 100ºC and 900ºC and of sample exposure time, and also enables multiple thermal desorption or pyrolysis to be performed on the same sample with accurate analysis of the compounds released from the sample at different temperatures (multi-shot). For our tests, an oxygen-free atmosphere was used that simulates the worst-case scenario in a ceramic kiln (fragmentation in reducing atmospheres).

Compound identification was achieved by selected ion monitoring (SIM) and by comparison with published mass spectra and spectral libraries (NIST11 and Wiley7).

The instrument was configured to detect generated compounds with a molecular weight greater than 50 m/z, so that certain compounds of interest, mainly formaldehyde, fall outside this unit's study range and need to be evaluated via other techniques.

3. RESULTS

Once testing parameters had been optimised, over 50 samples were analysed under the pre-set conditions, including a wide spectrum of products that comprised both solvent-borne and water-borne substances, as well as samples embedded in ceramic matrices, to assess their possible catalytic effects.

This paper describes the results obtained from 15 of the samples tested and include solvent-based and water-based samples.

The sample group includes products that were externally evaluated in industrial tests with optimal results in terms of emissions and odour, so our confirmation of those results with this technique underlines the earlier conclusion regarding the usefulness of analytic pyrolysis as a comparative tool.

After these samples had been subjected to the test conditions described, the following pyrograms were obtained:

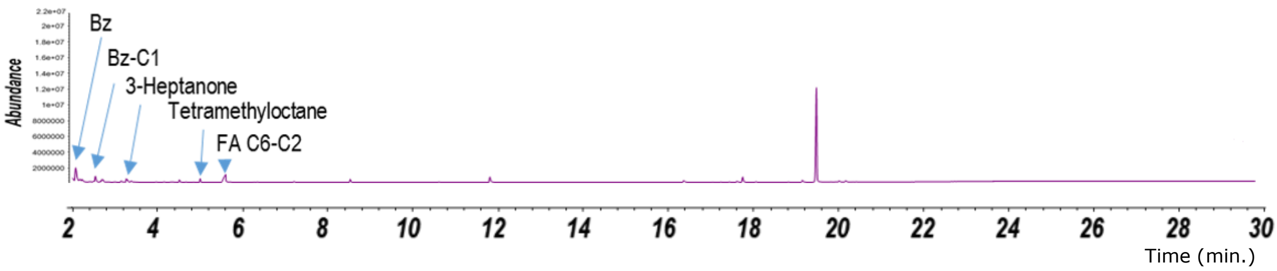


Fig. 4. *SAMPLE 1 pyrogram*

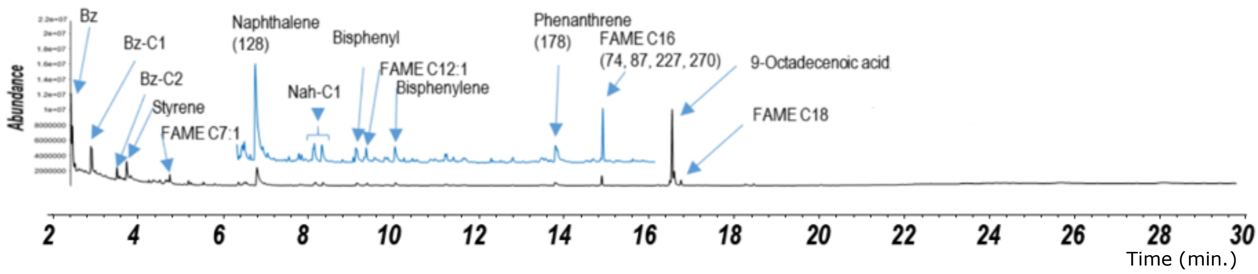


Fig. 5. *SAMPLE 2 pyrogram*

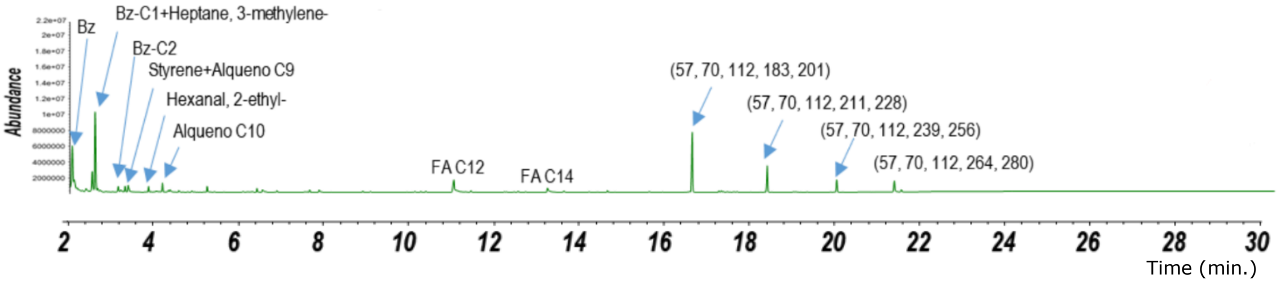


Fig. 6. *SAMPLE 3 pyrogram*

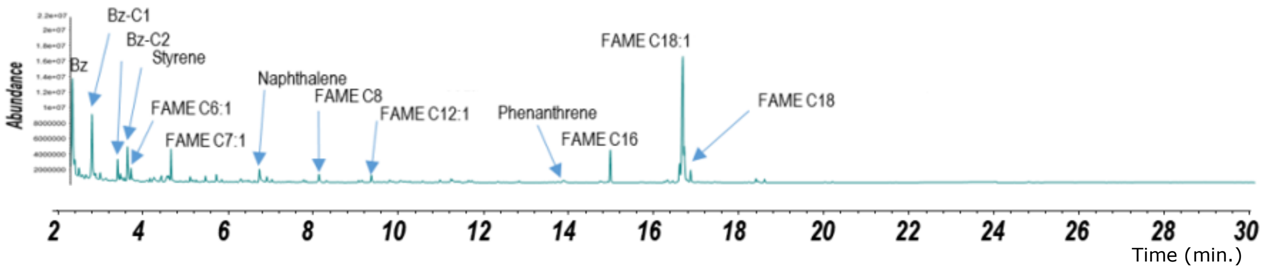


Fig. 7. *SAMPLE 4 pyrogram*

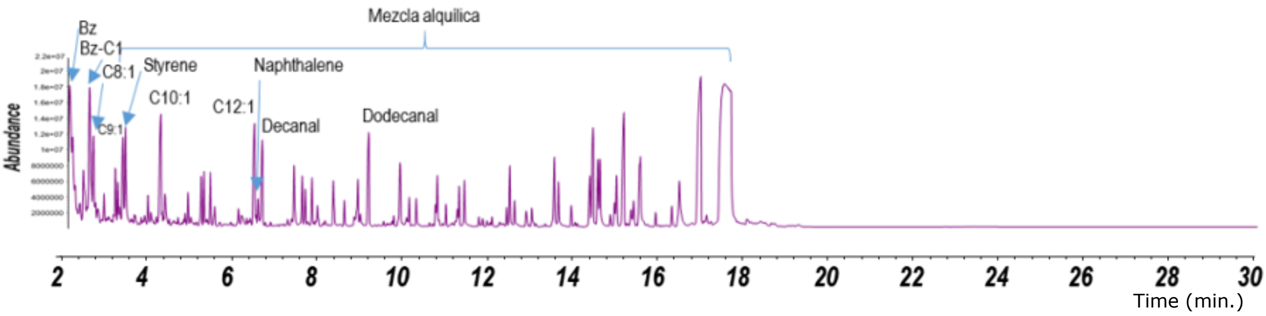


Fig. 8. *SAMPLE 5 pyrogram*

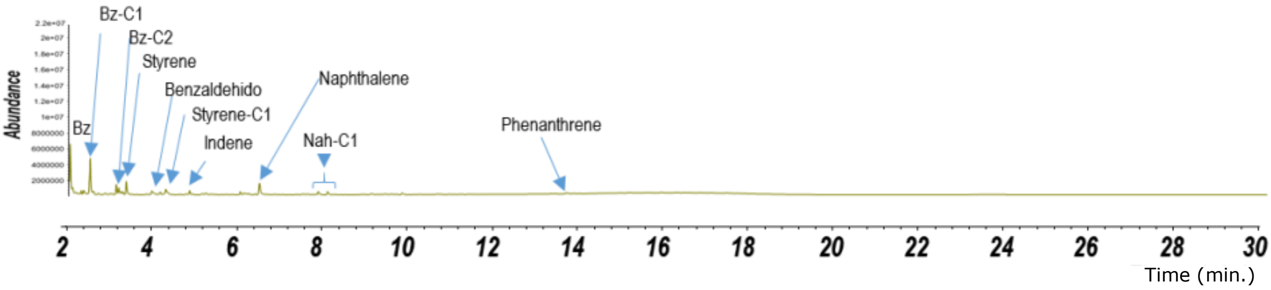


Fig. 9. *SAMPLE 6 pyrogram*

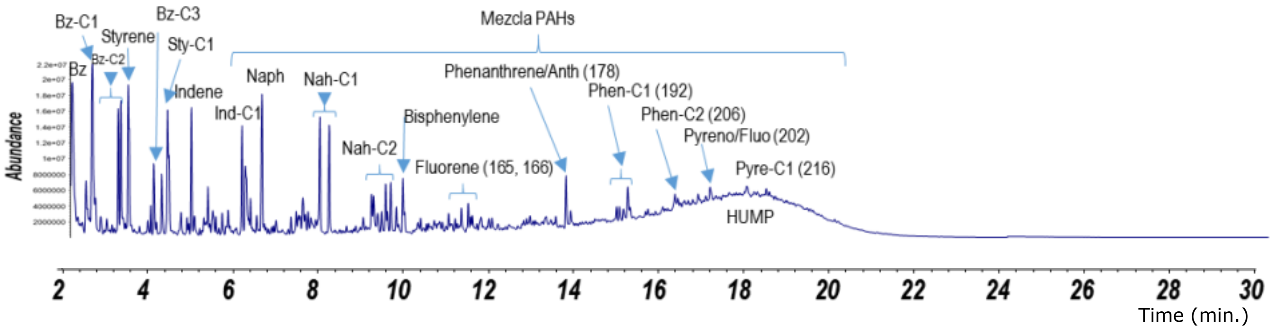


Fig. 10. *SAMPLE 7 pyrogram*

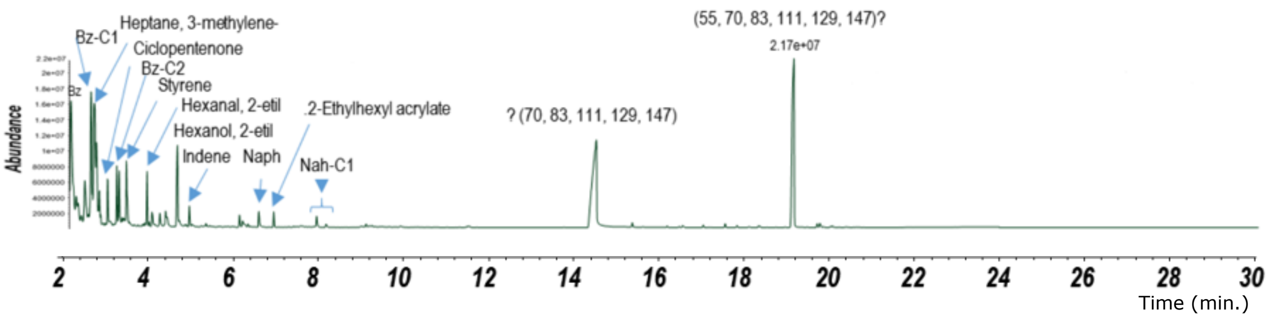


Fig. 11. *SAMPLE 8 pyrogram*

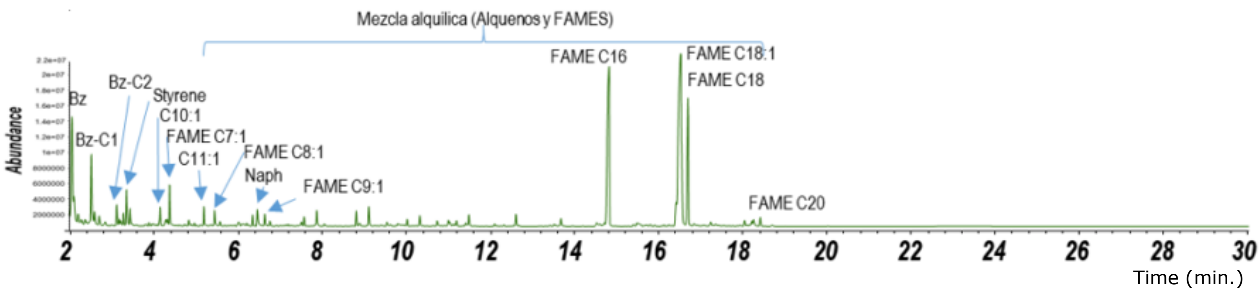


Fig. 12. *SAMPLE 9 pyrogram*

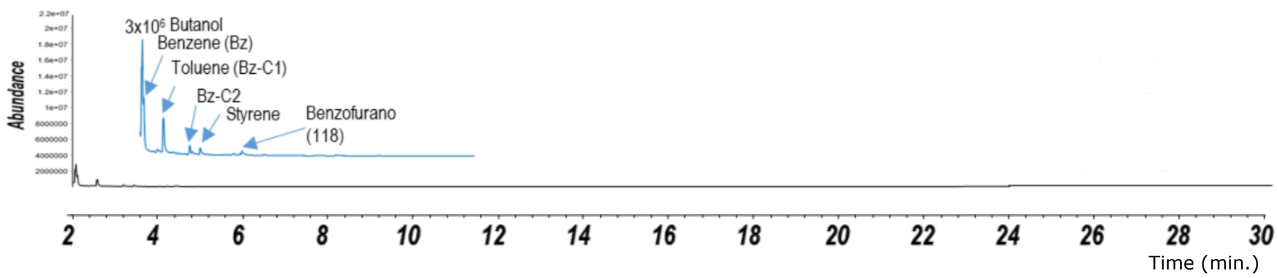


Fig. 13. *SAMPLE 10 pyrogram*

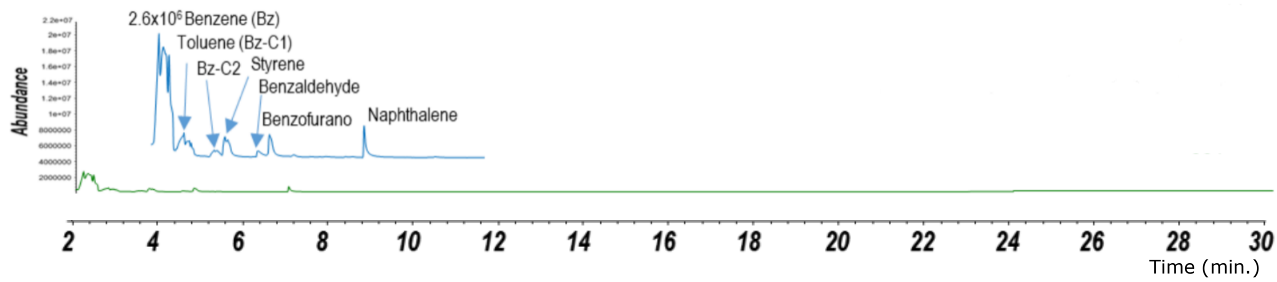


Fig. 14. *SAMPLE 11 pyrogram*

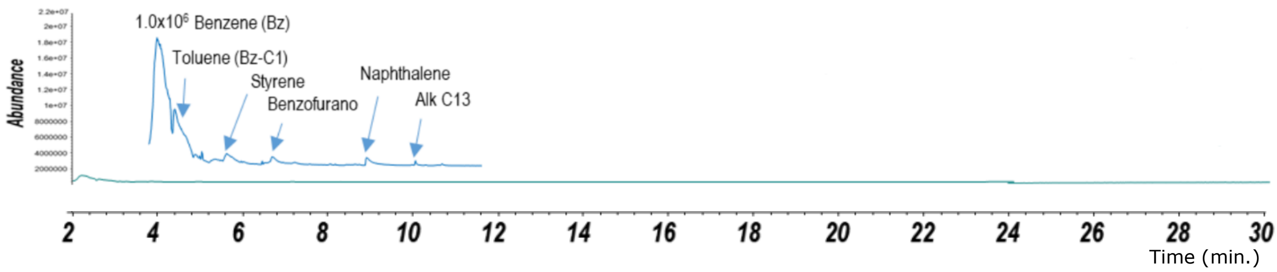


Fig. 15. *SAMPLE 12 pyrogram*

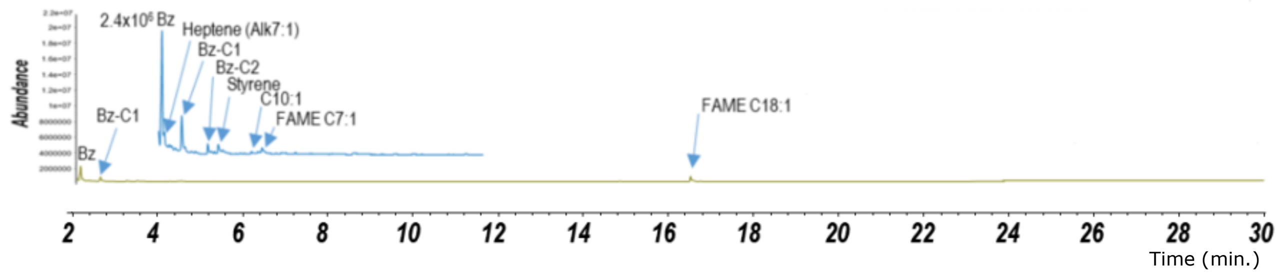


Fig. 16. *SAMPLE 13 pyrogram*

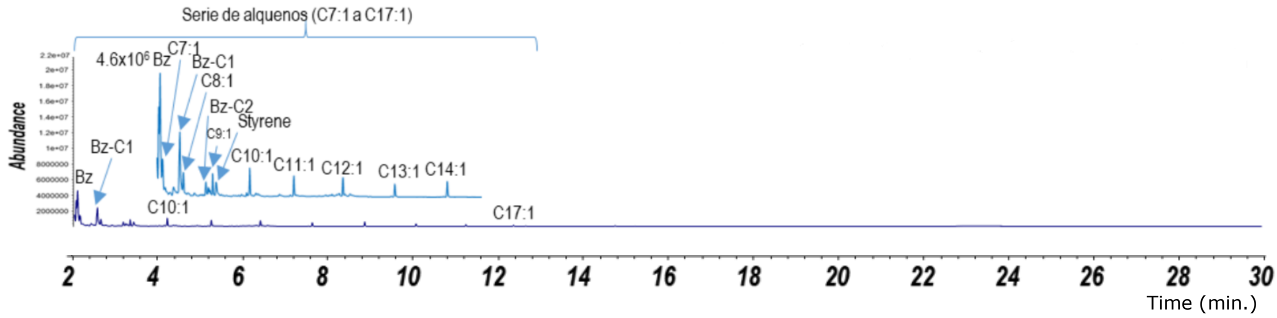


Fig. 17. *SAMPLE 14 pyrogram*

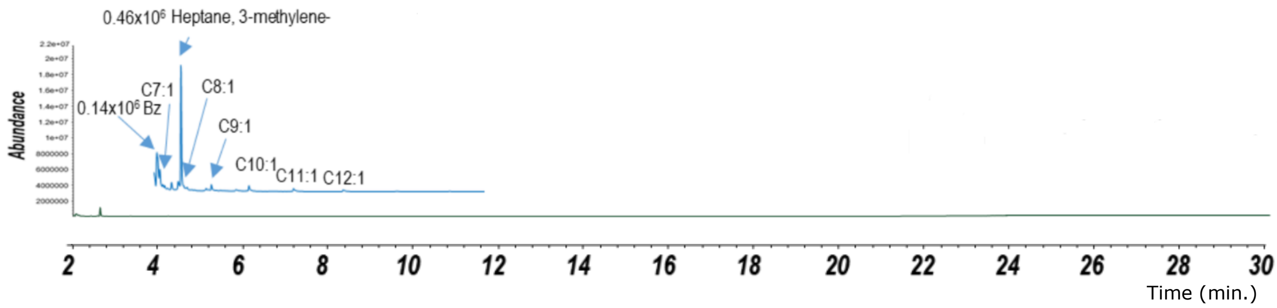


Fig. 18*. SAMPLE 15 pyrogram*

The above pyrograms display a series of signals based on the products detected in the various fragmentations that take place during the test. These signals are subsequently identified by GC/MS, as explained above.

As is evident from the various tests, the number of signals detected corresponding to the compounds generated vary notably between samples and a number of products can be seen with a high number of signals, which would suggest they are the ones to avoid in formulations.

It was noted that the signals detected after minute 15 are signals from remains of the original substance, so pyrograms should most effectively be studied over the 2-to-15-minute time-span.

On the basis of the above premises, a selection of study samples was made to perform more exhaustive analysis on those considered optimal, i.e., the ones that generated the least number of compounds. A semi-quantitative evaluation of the signals present was carried out on the basis of the area of peaks in the pyrograms and signals with a rating of less than 0.5% of the total area were discarded.

Once the selected products had been studied in detail, the compounds identified were compared against the CREL list (non-cancer Chronic Reference Exposure Levels), which sets exposure limits for certain substances classified as hazardous, below which surrounding populations are not considered to be at risk of undergoing cancer-producing effects when they are released into the air.

According to the nomenclature used, these compounds are:

BZ	*Benzene/alkyl benzenes*
ALK	*Alkane/Alkene*
PAH	*Aromatic polycyclic compounds*
ACRILATO	*Acrylate*
BZ-FURAN	*Furan benzene*
FA	*Fatty Acid*
FAME	*Fatty Acid Methyl Esters*
CET	*Ketone*
ETER	*Ether*
ALD	*Aldehydes*
PENTANONE	*Pentanone*

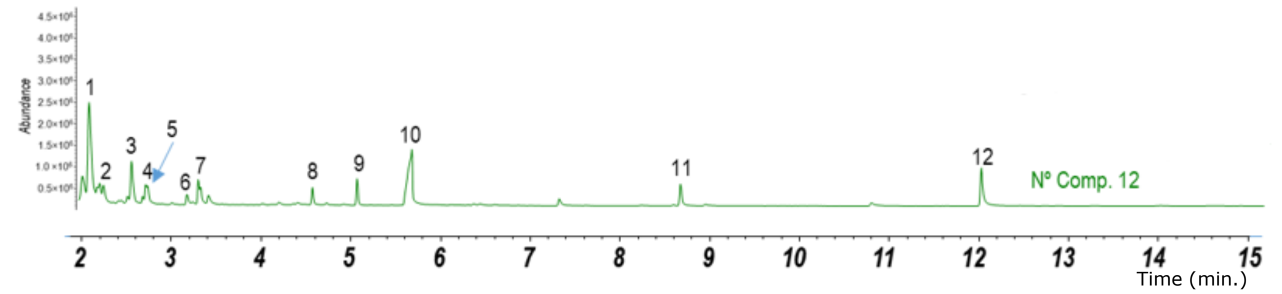
Table 2. *Nomenclature of detected compounds*

In short, the evaluation criteria that were established by this study include:

- Total number of peaks (compounds) in the pyrolysis chromatograph performed under the established test conditions.
- Only compounds that exceed 0.5% of the total area in the pyrograms are to be considered.
- Semi-quantitative evaluation of the identified peaks.

Based on the results obtained and the established criteria, 8 samples were determined as the best candidates for formulating inks with low emissions of potentially hazardous substances.

The results of these 8 samples are shown below.



Signal	Time	Absolute area	% area	Identification	Nomenclature
1	2,04	8,48	28,71	Benzene	BZ
2	2,15	0,55	1,85	1-Heptene	ALK
3	2,51	3,04	10,29	Benzene, methyl-	BZ
4	2,66	0,90	3,04	Butanoic acid, 2-methylene-, methyl ester	ACRILATO
5	2,68	1,07	3,63	2-Heptenal	CET
6	3,12	0,58	1,95	Ethylbenzene	BZ
7	3,24	1,86	6,29	3-Heptanone	CET
8	4,50	0,83	2,80	Methyl 1-Methyl-2-propenyl Ether	ETER
9	5,00	1,21	4,08	Octane, 3-methyl-	ALK
10	5,60	7,01	23,75	Hexanoic acid, 2-ethyl-	FA
11	8,57	1,31	4,42	Fragmentos m/z 171	
12	11,89	2,71	9,19	Fragmentos m/z 171	
		29,54	100,00		

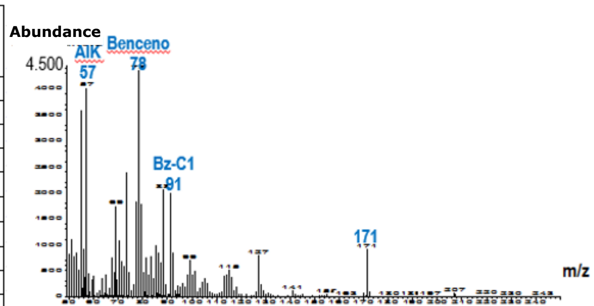
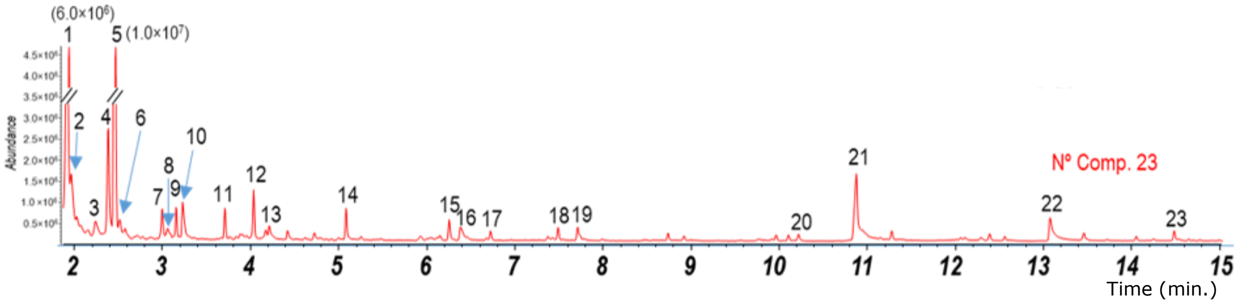


***Fig. 19**. Pyrogram, GC/MS and detected compounds, SAMPLE 1*



Signal	Time	Absolute area	% area	Identification	Nomenclature
1	2,04	10,61	21,50	Benzene	BZ
2	2,08	3,15	6,38	1-Heptene	ALK
3	2,36	1,40	2,84	Cyclohexane, methylene-	ALK
4	2,50	4,06	8,23	Benzene, methyl-	BZ
5	2,57	13,05	26,44	Heptane, 3-methylene-	ALK
6	2,63	0,91	1,84	1-Octene	ALK
7	3,11	1,05	2,12	Ethylbenzene	BZ
8	3,17	0,70	1,42	Benzene, 1,3-dimethyl-	BZ
9	3,27	0,96	1,95	1-Nonene	ALK
10	3,34	1,70	3,44	Styrene	BZ
11	3,81	0,80	1,63	Hexanal, 2-ethyl-	ALD
12	4,13	1,36	2,75	1-Decene	ALK
13	4,31	0,72	1,47	Benzofuran	BZ-FURAN
14	5,18	0,79	1,60	1-Undecene	ALK
15	6,34	0,57	1,16	1-Dodecene	ALK
16	6,47	0,66	1,34	Naphthalene	PAH
17	6,80	0,26	0,52	2-Ethylhexyl acrylate	ACRILATO
18	7,45	0,14	0,28	1-Tridecene	ALK
19	7,78	0,43	0,87	Undecanal	ALD
20	10,27	0,23	0,47	Tetradecanal	ALD
21	10,92	4,06	8,22	Dodecanoic acid	FA
22	13,10	1,50	3,03	Tetradecanoic acid	FA
23	14,50	0,24	0,49	2-Dodecen-1-al	ALD
		49,36	100,00		

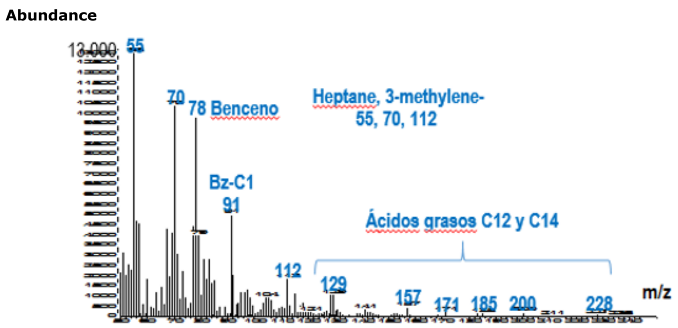


***Fig. 20**. Pyrogram, GC/MS and detected compounds, SAMPLE 3*

Signal	Time	Absolute area	% area	Identification	Nomenclature
1	2,03	38,73	76,62	Benzene	BZ
2	2,49	8,88	17,58	Benzene, methyl-	BZ
3	3,11	1,29	2,54	Benzene, 1,3-dimethyl-	BZ
4	3,35	1,65	3,25	Styrene	BZ
		50,55	100,00		

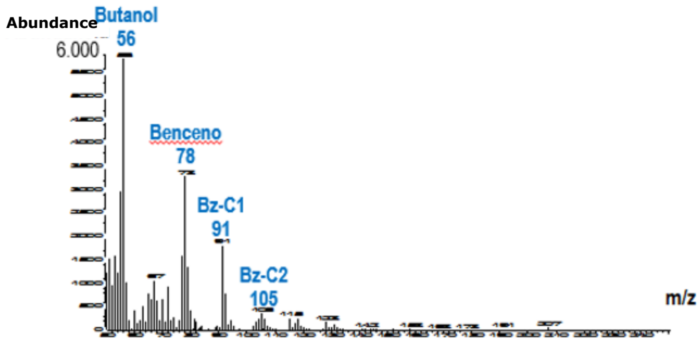
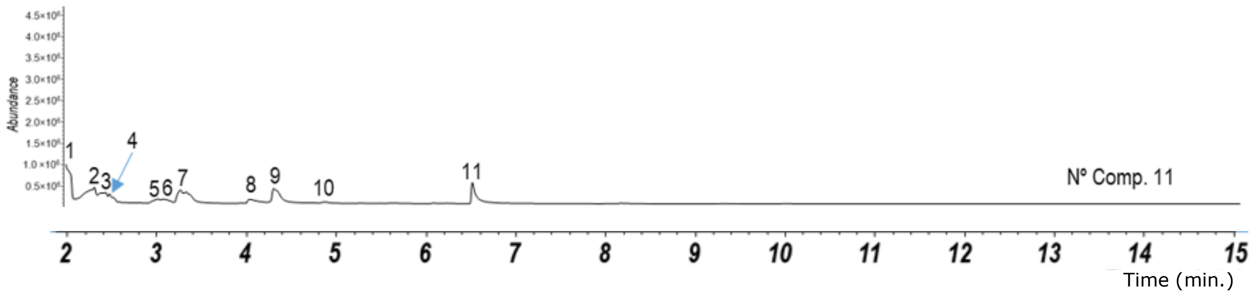


Fig. 21. *Pyrogram, GC/MS and detected compounds, SAMPLE 10*



Signal	Time	Absolute area	% area	Identification	Nomenclature
1	1,88	63,54	69,26	Benzene	BZ
2	2,23	6,17	6,72	Benzene, methyl-	BZ
3	2,36	3,05	3,33	Benzene, methyl-	BZ
4	2,40	1,83	2,00	Benzene, methyl-	BZ
5	2,94	0,97	1,06	Benzene, 1,3-dimethyl-	BZ
6	3,01	1,20	1,31	Benzene, 1,3-dimethyl-	BZ
7	3,26	5,60	6,10	Styrene	BZ
8	3,96	1,27	1,39	Benzaldehyde	BZ
9	4,24	3,90	4,25	Benzofuran	BZ-FURAN
10	4,80	0,26	0,29	Indene	PAH
11	6,45	3,93	4,29	Naphthalene	PAH
		91,74	100,00		

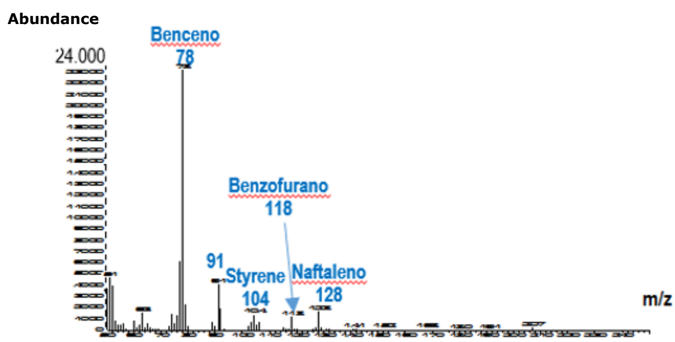
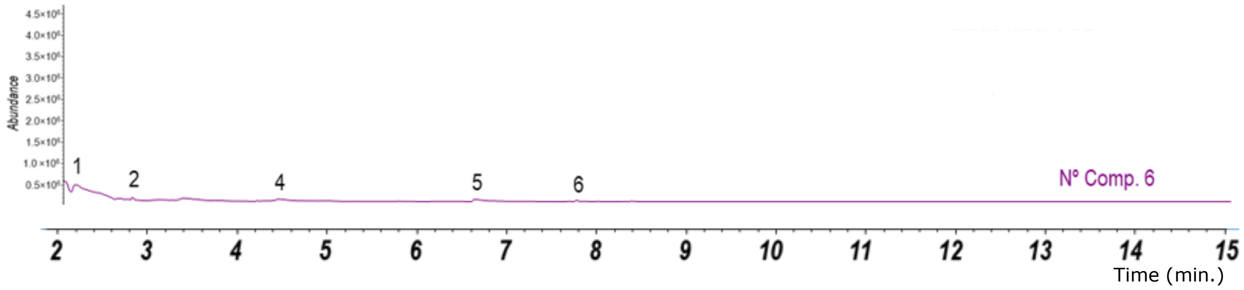


Fig. 22. *Pyrogram, GC/MS and detected compounds, SAMPLE 11*



Signal	Time	Absolute area	% area	Identification	Nomenclature
1	2,06	79,39	95,19	Benzene	BZ
2	2,69	0,77	0,92	Benzene, methyl-	BZ
3	3,27	0,79	0,94	Styrene	BZ
4	4,33	0,95	1,14	Benzofuran	BZ-FURAN
5	6,54	1,26	1,51	Naphthalene	PAH
6	7,67	0,26	0,31	Tridecane	ALK
		83,40	100,00		

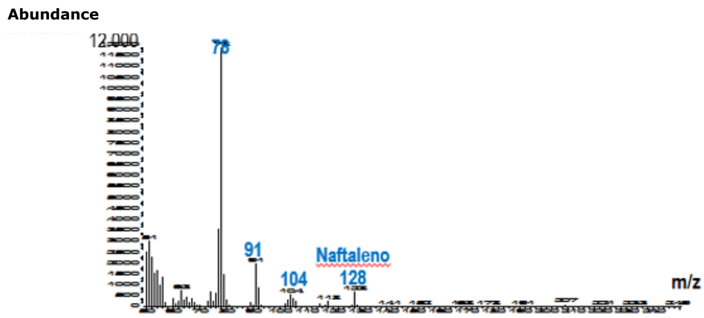
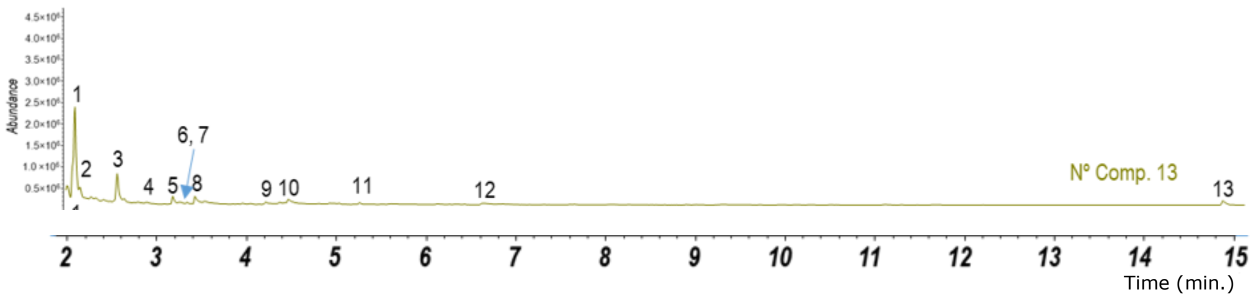


***Fig. 23**. Pyrogram, GC/MS and detected compounds, SAMPLE 12*



Signal	Time	Absolute area	% area	Identification	Nomenclature
1	2,02	23,14	46,36	Benzene	BZ
2	2,08	6,44	12,89	1-Heptene	ALK
3	2,49	7,71	15,44	Benzene, methyl-	BZ
4	2,57	1,96	3,92	1-Octene	ALK
5	3,11	1,61	3,23	Benzene, 1,3-dimethyl-	BZ
6	3,17	0,80	1,61	Benzene, 1,4-dimethyl-	BZ
7	3,27	0,45	0,90	1-Nonene	ALK
8	3,36	2,22	4,44	Styrene	BZ
9	4,15	0,73	1,46	1-Decene	ALK
10	4,39	2,53	5,07	6-Heptenoic acid, methyl ester	FAME
11	5,19	0,26	0,53	1-Undecene	ALK
12	6,55	0,64	1,29	Naphthalene	PAH
13	14,78	1,43	2,87	Hexadecanoic acid, methyl ester	FAME
		49,93	100,00		

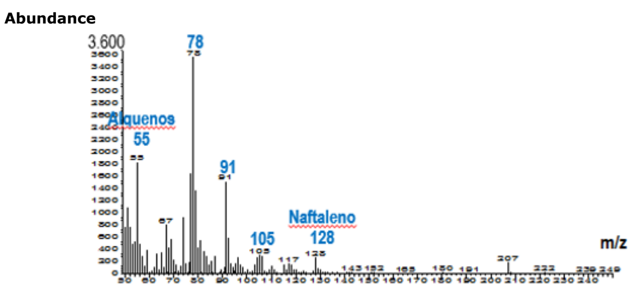
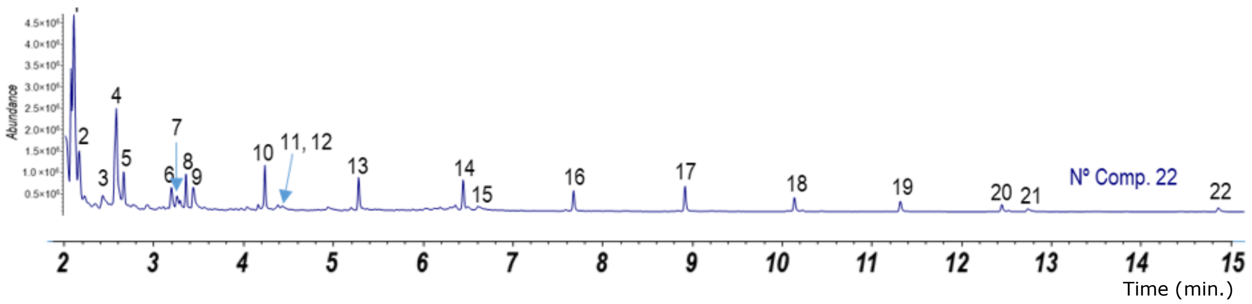


***Fig. 24**. Pyrogram, GC/MS and detected compounds, SAMPLE 13*



Signal	Time	Absolute area	% area	Identification	Nomenclature
1	2,01	15,44	34,40	Benzene	BZ
2	2,07	3,53	7,86	1-Heptene	ALK
3	2,33	1,70	3,78	1,3-Cycloheptadiene	ALK
4	2,48	6,95	15,48	Benzene, methyl-	BZ
5	2,57	2,42	5,40	1-Octene	ALK
6	3,10	1,25	2,78	Benzene, 1,3-dimethyl-	BZ
7	3,16	0,80	1,78	Benzene, 1,4-dimethyl-	BZ
8	3,26	1,51	3,36	1-Nonene	ALK
9	3,34	1,90	4,24	Styrene	BZ
10	4,13	1,93	4,30	1-Decene	ALK
11	4,28	0,43	0,96	Benzene, 2-propenyl-	BZ
12	4,33	0,48	1,06	Benzofuran	BZ-FURAN
13	5,18	1,16	2,58	1-Undecene	ALK
14	6,34	1,19	2,65	1-Dodecene	ALK
15	6,51	0,25	0,55	Naphthalene	PAH
16	7,56	0,84	1,88	1-Tridecene	ALK
17	8,80	1,08	2,42	1-Tetradecene	ALK
18	10,02	0,66	1,46	1-Pentadecene	ALK
19	11,20	0,47	1,05	1-Hexadecene	ALK
20	12,32	0,35	0,78	1-Heptadecene	ALK
21	12,62	0,26	0,58	Pentadecanal-	ALD
22	14,73	0,30	0,66	Heptadecanal	ALD
		44,88	100,00		

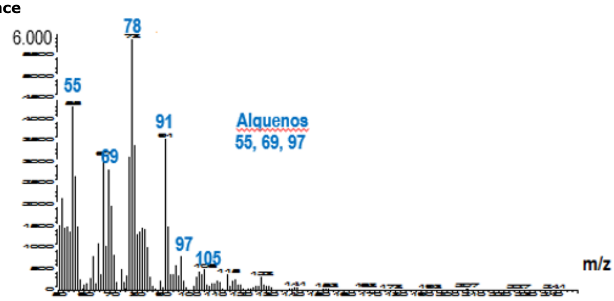
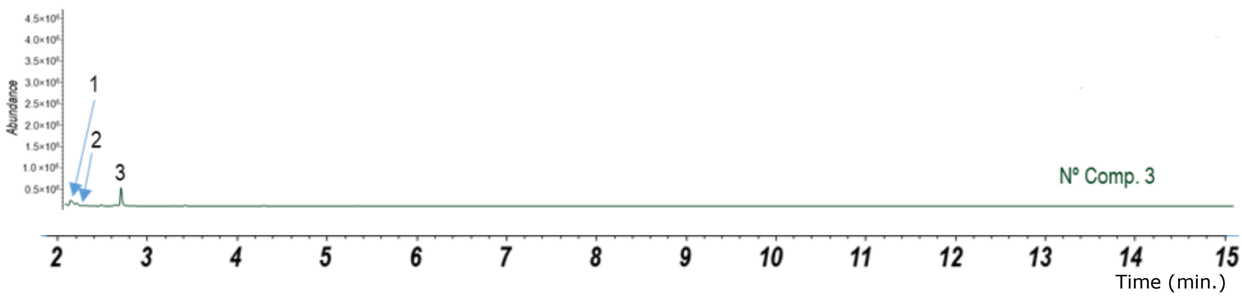


***Fig. 25**. Pyrogram, GC/MS and detected compounds, SAMPLE 1*



Signal	Time	Absolute area	% area	Identification	Nomenclature
1	1,98	10,57	31,21	Benzene	BZ
2	2,05	3,69	10,89	1-Heptene	ALK
3	2,55	19,60	57,89	Heptane, 3-methylene-	ALK
		33,86	100,0		

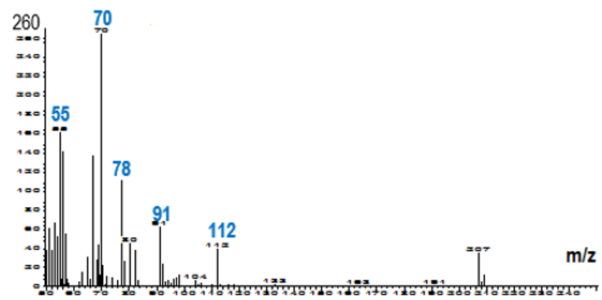


***Fig. 26**. Pyrogram, GC/MS and detected compounds, SAMPLE 15*

4. ASSESSMENT OF RESULTS

The tested samples were subjected to a final evaluation, taking into account the number of compounds and semi-quantification of the signals observed in the pyrogram, intensity in the GC/MS of the compounds detected, and their hazard rating according to the CREL list. It is important to note that all the tests were carried out with the same amount of sample, so the results are fully comparable between each other.

From all these results and by making a joint reading of the data obtained, a series of products of interest for the development of low-emission inks can be drawn up.

It is worth noting that this study has been able to demonstrate that ester, used from the outset by Colorobbia España, S.A., as the main base compound for its inks, obtained very good results in these tests compared to other similar products on the market.

5. CONCLUSIONS

As this study has proven, analytical pyrolysis is presented here as a precise, robust, reproducible and reliable technique for determining and identifying compounds generated during a firing process in the absence of oxygen. That makes it completely valid as a tool with which to compare different substances by their intrinsic properties and nature and thus select which products are most suitable for developing low-emission ceramic inkjet inks.

The results obtained need to be confirmed, not only by other techniques to back this study, but also through experimental tests at an industrial scale, since those conditions are unique in each case and will ultimately determine what products are generated.

Using the tool that has been presented here and which has served to confirm that Colorobbia's current inks deliver good environmental performance, a selection was made of optimal products that can be used as main solvents when developing new series of low-emission inks, appropriately adjusted to ensure our products maintain their usual quality standard.

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