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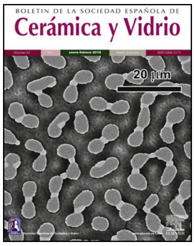

VOCs monitoring of new materials for ceramic tiles decoration: GC–MS analysis of emissions from common vehicles and inkjet inks during firing in laboratory

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ABSTRACT

The decoration of ceramic tiles "ink-jet revolution" has brought significant advantages to tiles manufacturing, but the explosive diffusion, until 4–5 years ago, of this technique has not been accomplished by an adequate scientific research. Among all the features that have to be studied yet, one of the most important is the influence of the new generation inks on the total emission at ceramic chimneys. In this paper, we present a first characterization of emissions from a set of commercial inks and vehicles: they were collected by propter firing of samples in an electric kiln and analyzed by GC–MS. This study is part of a larger research project, which includes the chemical characterization and the evaluation of thermal behavior of inks and vehicles by TG-DTA and other techniques. The obtained results permit to divide common vehicles into 3 classes, depending on their thermal behavior and emissions pattern. Inks, most of which present an ester based formulation, sometimes mixed with glycols or paraffins, follow the behavior of their single components. The most common formulation leads to the presence in the emission pattern of evaporation products (2-ethylhexyl esters of lauric, myristic, decanoic and octanoic acids) and decomposition products (mainly aldehydes and 2-ethyl-1-hexanol).

Monitorización de los COV de nuevos materiales para la decoración de azulejos cerámicos: análisis con GC-MS de las emisiones de vehículos comunes y de tintas digitales durante la cocción en laboratorio

Palabras clave:
Color
Pavimentos
Tintas digitales
Propiedades térmicas
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RESUMEN

La decoración de los azulejos cerámicos mediante tecnología Ink-jet ha supuesto numerosas ventajas en la producción de baldosas cerámicas, pero su rápida implantación no ha sido acompañada por una adecuada investigación científica, hasta hace 4–5 años. Entre todas las características que deberían ser estudiadas, una de las más importantes es la influencia de las nuevas tintas digitales en las emisiones totales de las chimeneas cerámicas. En este

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artículo presentamos una primera caracterización de las emisiones de un grupo de tintas y vehículos comerciales: las emisiones se recogieron durante la cocción en laboratorio y fueron analizadas por GC-MS. Este estudio es parte de una investigación más completa, que incluye la caracterización química y la evaluación del comportamiento térmico de tintas y vehículos por TG-DTA y otras técnicas. Los resultados permiten la clasificación de los vehículos más comunes en 3 clases, dependiendo de su comportamiento térmico y emisiones. La mayoría de las tintas que presentan una formulación a base de ésteres, algunas veces mezclados con glicoles o parafinas, siguen la conducta de cada uno de sus componentes. Las formulaciones más comunes presentan productos de evaporación (2-etilhexil ésteres de ácidos láurico, mirístico, decanoico y octanoico) y productos de descomposición (principalmente aldehídos y 2-etil-1-hexanol).

Introduction

From 2001, the ink-jet revolution in decoration technologies for ceramic tiles has started and nowadays it has become the most widespread technique [1].

This incredible success is due to its well-known pros, in comparison with traditional methods such rotary serigraphy and Rotocolor® systems: almost unlimited possibilities of decoration, reduced hazards of mechanical stress on unfired tiles, non-flat and expanded surfaces are now decorable, easier storage of decoration models, etc.

Before its introduction in ceramic industry, ink-jet technology had been already applied to other industrial applications (microchips, home printers, LCD and plasma screens, etc.).

Among the different methods of jetting, decoration of tiles is based on drop-on-demand (DOD) technique, where a software controls the deposition of inks drop by drop [2,3].

Digital inks for ceramic decoration are composed, until now, mainly of two phases: an inorganic pigment and an organic liquid phase.

Pigments (20–45% of the total weight) are usually crystalline ground compounds (metal aluminates, silicates or oxides), characterized by thermal stability up to 1200–1250 °C.

Pigment particles are kept in suspension by the liquid phase that must have also some specific rheological properties (high boiling point, low viscosity, etc.). This phase is divided in two main components: the vehicle (50–70% of the total weight) and the additives (5–10% of the total weight).

In spite of its success, ink-jet decoration has also some cons. For example, inks must have some restricted rheological properties to be jettable (diameter of pigment particles below 1 μm, surface tension between 20 and 45 mN/m, etc.) [4], at the same time, granulometry of pigments has to guarantee precise chromatic performances and avoid, as much as possible, sedimentation, which is generally more problematic to be overcome than in traditional inks.

As ink-jet decoration is a quite recent innovation for ceramic industry and according to the continuous and fast developments of this technique, until now scientific researches were focused just on few points, mainly related to rheological performances of inks [5,6].

For example, only during the last 2 years some studies on the chemical characterization of inks were proposed [7].

One of the most important aspect that still lacks a proper knowledge and comprehension, is how new digital ceramic inks contribute to emissions at chimneys, when they go through the firing processes of ceramic tiles. This problem has not to be underestimated because legislation regarding this matter is quite restrictive, at least in Italy, and understanding how new materials interact to modify gaseous emissions is fundamental to prevent and control the emission of potentially hazardous compounds.

Ceramic district of Sassuolo (Modena, Italy), for example, is under the control of ARPA Emilia-Romagna regulation that fixes specific limits for VOCs and aldehydes in emissions of ceramic industry [8].

Recently, Italian Confindustria Ceramica in collaboration with Centro Ceramico has published a report on the performances and environmental impact of producers of ceramic tiles between 2010 and 2013 [9]. This document underlines the increasing of VOCs in the period under consideration. Aldehydes, for example, have registered a significant increase in 2012 in complete manufacturing cycle, followed by a reduction in 2013, while in partial manufacturing cycles this value was still increasing in 2013. These are symptoms of changes in the ceramic industry, which may be linked to the introduction of new materials by inkjet technology.

Regardless of their growth, ARPA did not reported values higher than VOCs law limits, but some of these compounds (not fully identified yet) could be potentially irritating for throat, eyes or skin [10].

It is also necessary to take in consideration the particular conformation of ceramic kilns, which operate in counter-current [11]. This set-up implicates for tiles, with just printed inks on their surface, a thermal shock to even 500 °C while entering in the pre-kiln. These temperatures are obtained thanks the hot air coming from the firing sectors, which passes above tiles surface and goes directly toward the chimney. Inks can, so, have a combustive reaction and their products can be removed from tile surface and interact with molecules transported by the air flow, or inks can simply evaporate to the chimney.

In this paper, we present first results of our study on the characterization of gaseous emissions from a set of commercial inks and vehicles, submitted, in Lab., to a slow or industrial-like fast firing. This study is part of a wider research that is collecting data on thermal behavior, chemical

Table 1 – Sampled vehicles.

Vehicles	Samples
Isoparaffin oil	PRF1
n-Paraffin oil	PRF2
Tripropylene glycol *n*-butyl ether	TPnB
2-Ethylhexyl stearate	2-EHS
Ethylhexyl cocoate	EHC
Caprylic/capric triglyceride	CCT
2-Ethylhexyl laurate	2-EHL
Tripropylene glycol methyl ether	TPM

characterization and, of course, potentially polluting emissions of inks and common vehicles, to improve knowledge and comprehension of these materials.

Materials and methods

Samples and analytical procedure

We collected 55 inks (named I1, I2, . . ., I55) and 8 common vehicles (named as in Table 1) from inks suppliers in the ceramic district of Sassuolo (Modena, Italy). For the most of inks, no information was given about their composition. Vehicles are commercial products, with potentially low degree of purity.

Each sample was first characterized by infrared spectroscopy (FTIR) and thermogravimetric analysis coupled with differential thermal analysis (TG-DTA), in order to understand at least the class of the main organic compounds and their thermal behavior. The description of FTIR and TG-DTA procedures, as well as results of these two preliminary steps for vehicles and for the first 39 inks, have already been published [12].

Then, to study polluting products, samples have been fired in an electric tubular kiln and their gaseous emissions have been collected by Tenax TA tubes and analyzed in a GC–MS equipment.

Vehicles have been also characterized by direct injection in GC–MS to verify their purity, but results will not be discussed in detail in this paper.

Sampling of emissions

A known quantity of sample (10 mg of ink, or 5 mg of vehicle) was loaded in a quartz holder and inserted in an electric tubular kiln (Carbolite STF 15/50/450), equipped with a Quartz tube of internal diameter of 1 cm. Then, samples were heated with the following temperature program: from ambient temperature to 800 °C in 15 min, dwell at 800 °C for 10 min.

During the whole heating program, air was pumped through the kiln to a flow splitter with 4 exits, at the end of the kiln tube. Each exit can be equipped with a sampling tube or used as flow regulator. Each flow of air through tubes can be adjusted separately, for a total air flow of 1 l/min.

For the first qualitative screening of VOCs, Tenax TA (Supelco 60/80, glass tube, ¼ in. OD × 4 mm ID × 7 in.) has been selected to collect air samples, because of its property and affinity to a wide range of VOCs [13–16]. Air through Tenax tube was set to 200 ml/min. Tenax tubes were immediately analyzed with the next steps, or stored in closed boxes, avoiding light interaction, until their analysis.

Table 2 – Classification of inks by FTIR and comparison with vehicles.

Main vehicle class	Inks
Esters	I1, I3, I4, I5, I6, I8, I11, I12, I13, I14, I16, I18, I19, I20, I21, I22, I26, I27, I28, I29, I30, I31, I32, I33, I34, I35, I36, I37, I38, I39, I43, I44, I51, I53
Glycols	I23, I41, I42, I52
Paraffins	I2, I7, I10, I15
Glycols + esters	I9, I50, I54, I55
Paraffins + esters	I24, I25
Water + glycols	I17, I40, I45, I46, I47, I48, I49

Desorption and GC–MS analysis

One of the most useful characteristic of Tenax is its desorption procedure. After sampling, tubes were desorbed in a thermal desorption system (TDS), molecules were cryo-focused at −140 °C with a cooled injection system (CIS) and, then, were sent to a gas chromatograph coupled with a mass spectrometer. Desorption and separation parameters have been selected on the basis of literature [16–18] and previous tests.

TDS starting temperature was set at 40 °C, after 0.50 min temperature was raised to 270 °C at 60 °C/min and maintained for 10 min. Desorption was carried on with helium at 40 ml/min, in splitless mode.

CIS was kept at −140 °C with liquid nitrogen for all the desorption step, then temperature was rapidly raised to 280 °C at 12 °C/s and maintained for 2 min.

Inlet was set to solvent vent mode, purged at 900 ml/min after 0.40 min and kept at 250 °C.

Desorbed molecules were then directed to the GC–MS (Agilent 6890N), equipped with a Restek RXi-1MS column (60 m × 250 μm × 1 μm). Oven initial temperature was kept at 35 °C for 4 min, then raised to 150 °C at 3 °C/min, and finally to 270 °C at 8 °C/min. The final temperature was maintained for 20 min. Carrier gas was helium at 1 ml/min.

MS operated in scan mode, in the range 15–450 *m*/*z*.

Results and discussion

For the extensive results of FTIR and TG-DTA, we refer to our previous paper [12]. On the basis of FTIR data, we divided our samples in 6 general groups, depending on the main classes of compounds identified and on the comparison to vehicles data. This classification has been revised and corrected after the emissions study and the new inks samples have been added (Table 2).

GC–MS

Emissions of vehicles

Referring to the emissions of vehicles, all the identified compounds are listed in Table 3 .

According to their thermal behavior, PRF1 and PRF2 are characterized mainly by evaporation products. Unfortunately, hydrocarbons peaks are often not well separable, so, especially

Table 3 – Identified compounds in vehicles emissions.

Compounds	2-EHS	EHC	CCT	2-EHL	EHP	TPM	TPnB	PRF1	PRF2
Aldehydes									
Butanal	X		X				X		
Pentanal	X	X	X	X	X				
Hexanal	X	X	X	X	X	X			
Heptanal	X		X	X	X				
Hexanal, 2-ethyl-	X			X	X				
2-Hexanal, 2-ethyl-	X								
Octanal	X	X	X	X	X				
Nonanal	X		X	X	X				
Decanal	X			X	X				
Undecanal	X								
Dodecanal	X								
Tridecanal	X				X				
2-decenal, (E)-		X							
Ketones									
2-Pentanone	X		X						
2-Hexanone	X		X						
3-Hexanone, 5-methyl-	X								
2-Heptanone			X						
3-Heptanone	X								
2-Octanone	X		X	X	X				
2-Nonanone	X		X	X	X				
2-Decanone	X			X	X				
2-Undecanone	X				X				
2-Dodecanone	X				X				
2-Tridecanone					X				
Glycols and glycol ethers									
Tripropylene glycol monomethyl ether (isomers)	X		X			X	X		
2-Propanol, 1-[1-methyl-2-(2-propenyloxy)ethoxy]-			X						
Ethanol, 2-(1,1-dimethylethoxy)-					X				
Hexaethylene glycol dimethyl ether					X				
Tri(1,2-propyleneglycol), monomethyl ether					X				
Propylene glycol monobutyl ether							X		
Dipropylene glycol (isomers)							X		
Tripropylene glycol *n*-butyl ether	X		X				X	X	
Organic acids									
Octanoic acid			X						
Nonanoic acid	X		X		X				
n-Decanoic acid	X		X						
Undecanoic acid	X								
Dodecanoic acid				X	X				
n-Hexadecanoic acid	X								
Alcohols									
1-Hexanol, 2-ethyl-	X	X		X		X			
Propanoic acid, 2,2-dimethyl-							X		
Dioxolanes									
1,3-Dioxolane, 2-ethyl-4-methyl-							X		
Linear alkanes									
Hexane	X		X	X	X				
Heptane	X		X	X	X				
Octane	X		X						
Nonane	X		X						
Decane	X				X				
Undecane	X								

Table 3 – (*Continued*)

Compounds	2-EHS	EHC	CCT	2-EHL	EHP	TPM	TPnB	PRF1	PRF2
Dodecane	X			X	X				
Tridecane	X								
Tetradecane	X				X	X			X
Pentadecane	X				X	X			X
Hexadecane	X								X
Heptadecane	X								X
Octadecane									X
Nonadecane									X
Eicosane									X
Branched alkanes									
Heptane, 3-methyl-	X								
Nonane, 2-methyl-5-propyl-								X	
Dodecane, 3-methyl-								X	
Dodecane, 2,6,10-trimethyl-								X	X
Dodecane, 2,7,10-trimethyl-								X	
Dodecane, 2,2,11,11-tetramethyl-								X	
Tetradecane, 2,6,10-trimethyl-									X
Pentadecane, 2-methyl-									X
Pentadecane, 2,6,10-trimethyl-									X
Pentadecane, 2,6,10,14-tetramethyl-								X	
Hexadecane, 2-methyl-									X
Hexadecane, 3-methyl-									X
Hexadecane, 4-methyl-									X
Hexadecane, 2,6,10-trimethyl-									X
Hexadecane, 2,6,10,14- tetramethyl-								X	X
Heptadecane, 2-methyl-									X
Heptadecane, 4-methyl-									X
Heptadecane, 2,3-dimethyl-									X
Octadecane, 3-methyl-									X
Nonadecane, 9-methyl-								X	
Cyclic alkanes									
Cyclohexane						X			
Lactones									
Butyrolactone			X						
γ-Heptalactone			X						
γ-Octalactone			X						
δ-Octalactone			X						
γ-Decalactone			X						
δ-Decalactone			X						
γ-Undecalactone			X						
Alkenes									
Heptane, 3-methylene-	X	X		X	X				
1-Nonadecene									X
Fatty acids esters									
Acetic acid, 2-ethylhexyl ester	X								
n-Butyric acid 2-ethylhexyl ester	X				X				
Pentanoic acid, 2-ethylhexyl ester	X				X				
Hexanoic acid, 2-ethylhexyl ester	X				X				
Octanoic acid, 2-ethylhexyl ester		X			X	X	X		
Decanoic acid, 2-ethylhexyl ester		X			X				
Lauric acid, 2-ethylhexyl ester		X	X		X	X			X
Myristic acid, 2-ethylhexyl ester		X	X						
Palmitic acid, 2-ethylhexyl ester					X				
Hexanedioic acid, bis(2-ethylhexyl) ester									X
Octanoic acid, methyl ester			X						
Decanoic acid, methyl ester			X						
Octanoic acid, 2-propenyl ester			X						
Butyl formate							X		
Butyl caprate			X						

Table 3 – (*Continued*)

Compounds	2-EHS	EHC	CCT	2-EHL	EHP	TPM	TPnB	PRF1	PRF2
Butyl caprylate			X						
Butyl palmitate					X				
n-Capric acid isopropyl ester				X					
Myristic acid, isopropyl (o 1-methylethyl) ester				X					
Palmitic acid, isopropyl (o 1-methylethyl) ester				X					
Stearic acid, isopropyl (o 1-methylethyl) ester				X					
Lauric acid, 1-methylethyl ester	X	X	X	X			X		
Elaidic acid, 1-methylethyl ester (o isopropyl)				X					
Heptanoic acid, 4-octyl ester					X				
Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester						X	X		
Glycerol tricaprylate				X					

in PRF1 the univocal identification of peaks has been difficult and, for most of the peaks, impossible. Anyway, the MS pattern of some branched alkanes can be recognized between principal compounds, among which 2,6,10,14-tetramethylpentadecane is identifiable, for example.

PRF2 emissions are characterized by the same mixture of linear and branched alkanes (with chains from C_{12} to C_{20}) found by direct injection.

In TPM emissions, we can recognize evaporation products as well (tripropylene glycol monomethyl ether), with some impurities, due to the not high purity of the commercial product and to residues in the GC column.

TPnB emissions seems to confirm the thermal behavior recognized by TG-DTA, with a weak exothermic peak after the main endothermic phenomenon. Its main emission is tripropylene glycol *n*-butyl ether, indeed, but some decomposition compounds as dipropylene glycol, tripropylene glycol monomethyl ether or unsaturated glycols are present [19–21].

Same considerations can be done for 2-EHL. The analysis of the liquid vehicle revealed that the main compound was not 2-ethylhexyl laurate, as it has been claimed, but 1-methylethyl laurate (1-MEL). The same ester is the main emission product, due to evaporation. Secondary components, as lauric acid, comes from the decomposition of 1-MEL, while 1-methylethyl esters of heavier fatty acids (C_{14}–C_{18}) could be impurities.

EHC is a mixture of 2-ethylhexyl esters of C_8, C_{10}, C_{12}, C_{14}, C_{16} fatty acids, that are present as evaporation products in EHC emissions. The fast firing of EHC causes also the decomposition of some molecules into aldehydes (pentanal, hexanal, octanal, nonanal), 2-ethyl-1-hexanol and other light compounds.

Sample 2-EHS has been revealed to be not pure 2-ethylhexyl stearate, but a mix of this ester with 2-ethylhexyl palmitate. The chromatogram of 2-EHS emissions highlights the predominance of decomposition phenomena (identified as exothermic events by TG-DTA) that 2-EHS meets with. The most abundant compound is 2-ethyl-1-hexanol, from the cracking of 2-ethylhexyl esters. Various aldehydes, organic acids, ketones and hydrocarbons complete the emission chart, underlining the uncomplete combustion of 2-EHS due to the removal of intermediate products from the reaction site by the air flow [22].

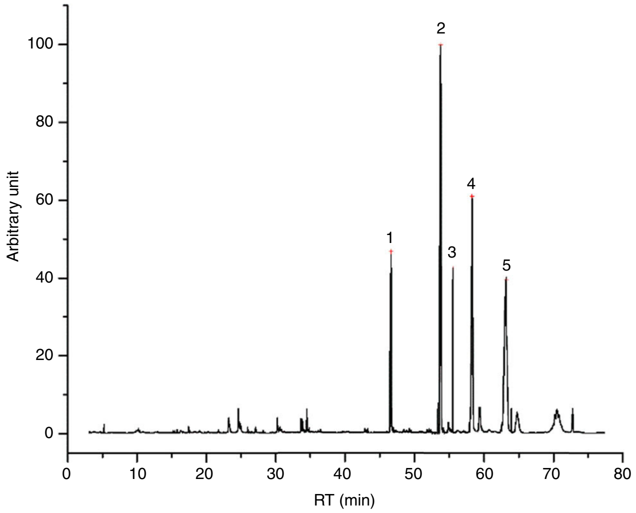

Fig. 1 – I23 chromatogram – (1) 1,1′-[(1-methyl-1,2-ethanediyl)bis(oxy)]bis-2-propanol, (2) tripropylene glycol *n*-butyl ether, (3) 1-methylethyl laurate, (4) and (5) ? = unidentified compound.

CCT is composed mainly of glycerol tricaprylate. We found it also in CCT emissions, but just as minor component. In fact, the chromatogram of CCT emissions presents numerous substances, coming from the exothermic decomposition of glycerol tricaprylate. Among these, aldehydes, ketones, fatty acids esters (especially, different esters of octanoic acid, not always perfectly identifiable), some glycol ethers, and lactones. Some studies, for example, have demonstrated that lactones form spontaneously from triglycerides, from the hydroxy-fatty acids liberated by heating [23]. Selke et al. identified the same classes of compounds as products of the thermal oxidation of tristearin [24] and triolein [25].

Emissions of inks

Glycol based inks (4/55), like I23 (Fig. 1), are characterized mostly by evaporation products, tripropylene glycol monomethyl ether and tripropylene glycol *n*-butyl ether above all. We found also few aldehydes and dioxolanes, as well as some lighter glycol ethers, deriving from the decomposition

Table 4 – Identified compounds in I23 emissions.

RT (min)	Compound
15.218	1,3-Dioxane, 2-methyl-
15.795	1,3-Dioxolane, 2,2-dimethyl-
17.422	Formic acid, butyl ester
21.741	Hexanal
23.228	2-Propanone, 1-(acetyloxy)-
24.609	1-Methoxy-2-propyl acetate
25.935	1-Methoxy-2-propyl acetate
27.080	Heptanal
30.229	?
33.654	Dipropylene glycol monomethyl ether
33.865	Dipropylene glycol monomethyl ether
34.503	Dipropylene glycol monomethyl ether
34.854	Dipropylene glycol monomethyl ether
36.471	Isobutyl ether
46.500	Dipropylene glycol
46.641	Dipropylene glycol
53.371	Tripropylene glycol *n*-butyl ether
53.632	Tripropylene glycol *n*-butyl ether
53.732	Tripropylene glycol *n*-butyl ether
53.813	Tripropylene glycol *n*-butyl ether
55.520	Dodecanoic acid, 1-methylethyl ester
63.947	Glycol (?)
72.811	Hexanedioic acid, bis(2-ethylhexyl) ester

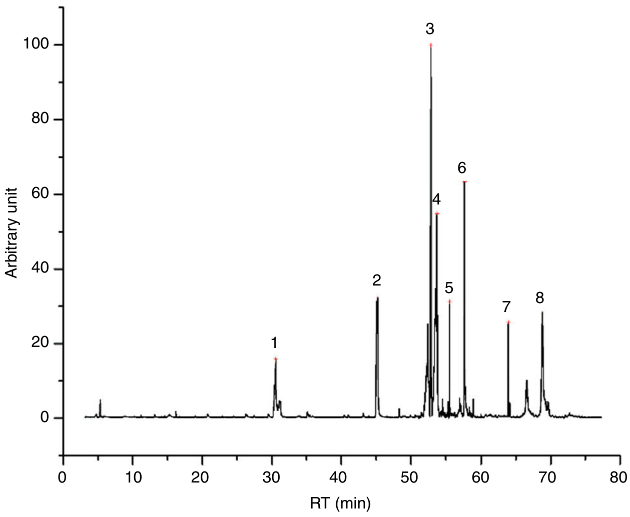

Fig. 2 – I49 chromatogram – (1) diethylene glycol, (2) triethylene glycol, (3) tetraethylene glycol, (4) butylated hydroxytoluene, (5) 1-methylethyl laurate, (6) pentaethylene glycol, (7) 2-ethylhexyl ester laurate and (8) 2-ethylhexyl ester laurate.

Table 5 – Identified compounds in I49 emissions.

RT (min)	Compound
5.304	Water
11.200	1,3-Dioxolane
13.148	1,3-Dioxolane, 2-methyl-
16.192	1,4-Dioxolane
26.251	?
29.475	?
30.555	Diethylene glycol
35.105	1,3-Dioxan-5-ol
43.125	Octanoic acid
45.059	Triethylene glycol
45.224	Triethylene glycol
48.268	Triethylene glycol
52.843	Tetraethylene glycol
53.692	Butylated hydroxytoluene
53.792	?
55.515	Dodecanoic acid, 1-methylethyl ester
57.659	Pentaethylene glycol
58.342	1-Decanol, 2-hexyl-
58.915	Heptaethylene glycol
63.942	Lauric acid, 2-ethylhexyl ester
64.148	Fatty acid ester?
68.828	Octadecanoic acid, octylester

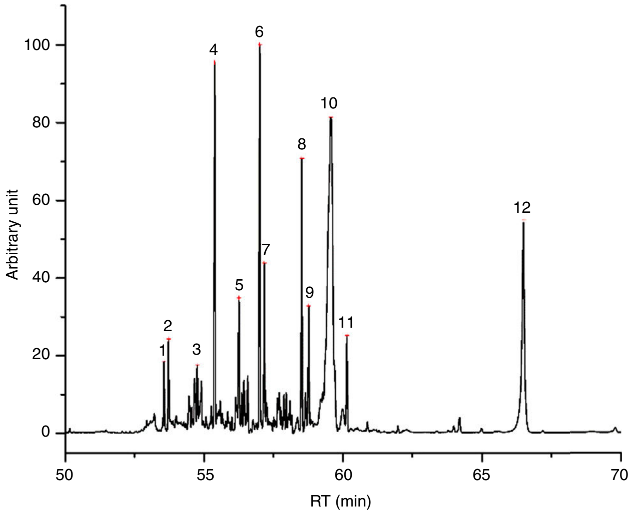

Fig. 3 – I2 chromatogram – (1) pentadecane, (2) butylated hydroxytoluene, (3) 2-methyl-pentadecane, (4) hexadecane, (5) 2,6,10-trimethyl-pentadecane, (6) ?, (7) 2,6,10,14-tetramethyl-hexadecane, (8) octadecane, (9) 2,6,10,14-tetramethyl-hexadecane, (10) ?, (11) eicosane and (12) 1,2-diethyl-cyclohexadecane.

of the main components. I23 DTA shows two events, indeed. The first one, endothermic, could be the evaporation of glycols; the second one, exothermic, could confirm the decomposition of evaporation products. In Table 4 all the identified compound in I23 emission are reported.

Water + glycol based inks (7/55), of which I49 is an example (Fig. 2), release less quantity of substances, being equal the weight in comparison with another type of ink. Their chromatograms display the evaporation products from the glycol part, which of course depend on the chosen glycol. I49, for instance, seems to be a mix of triethylene, tetraethylene and pentaethylene glycols, to which a fraction of esters is added. In the first part of the chromatogram, there are some weak peaks recognized as dioxolanes, therefore the same considerations already done for I23 are valid for I49 too. Table 5 shows the characterization of I49 emissions.

Also paraffin based inks (4/55), as I2 (Fig. 3) show mainly compounds coming from evaporation, confirming the behavior registered for PRF1 and PRF2. Their emissions are characterized by C_{14}–C_{20} alkanes, linear or branched. All the inks of this group are also characterized by the presence of some light aldehydes and carboxylic acids (octanoic

Table 6 – Identified compounds in I2 emissions.

RT (min)	Compound
15.514	Pentanal
21.785	Hexanal
27.163	Heptanal
28.207	Heptanal
33.976	Octanal
35.106	2H-pyran-2-one, tetrahydro-
37.135	2-Octenal, (E)-
37.893	Heptanoic acid
40.012	Nonanal
42.914	2-Nonenal, (E)-
43.185	Octanoic Acid
45.138	Decanal
46.514	Dipropylene glycol
46.654	1-Propanol, 2-(2-hydroxypropoxy)-
47.142	2-Decenal, (E)-
48.939	Tridecane
49.928	*n*-Decanoic acid
50.159	2-Tridecenal, (E)-
53.558	Pentadecane
53.719	Butylated hydroxytoluene
54.558	Tridecane, 5-methyl-
54.658	Pentadecane, 4-methyl-
54.753	Pentadecane, 2-methyl-
54.899	Tetradecane
55.381	Hexadecane
56.250	Pentadecane, 2,6,10-trimethyl-
56.350	Hexadecane, 4-methyl-
56.431	Hexadecane, 2-methyl-
56.566	Hexadecane, 3-methyl-
56.998	Heptadecane
57.164	Hexadecane, 2,6,10,14-tetramethyl-
57.887	Heptadecane, 2-methyl-
57.967	Heptadecane, 2-methyl-
58.524	Octadecane
58.660	Isopropyl myristate
58.775	Hexadecane, 2,6,10,14-tetramethyl-
59.564	?
60.146	Eicosane
60.879	Nonadecane, 9-methyl
61.979	Linear alkane
64.193	?
66.498	Cyclohexadecane, 1,2-diethyl-

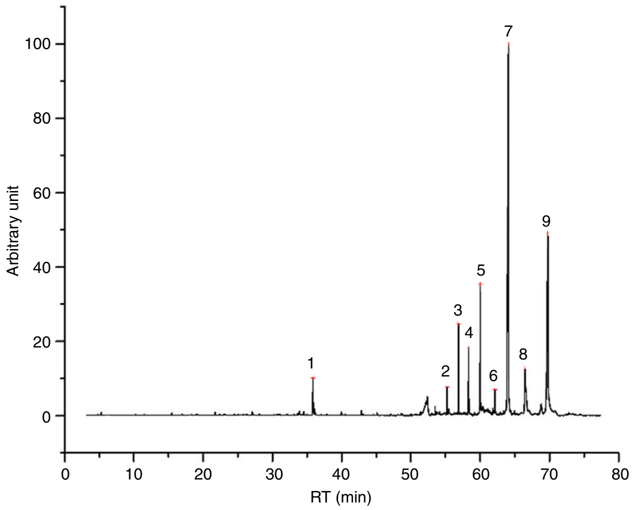

Fig. 4 – I33 chromatogram – (1) 2-ethyl-1-hexanol, (2) ?, (3) 2-ethylhexyl octanoate, (4) 2-hexyl-1-decanol, (5) 2-ethylhexyl decanoate, (6) ?, (7) 2-ethylhexyl ester laurate, (8) 1-eicosene and (9) 2-ethylhexyl myristate.

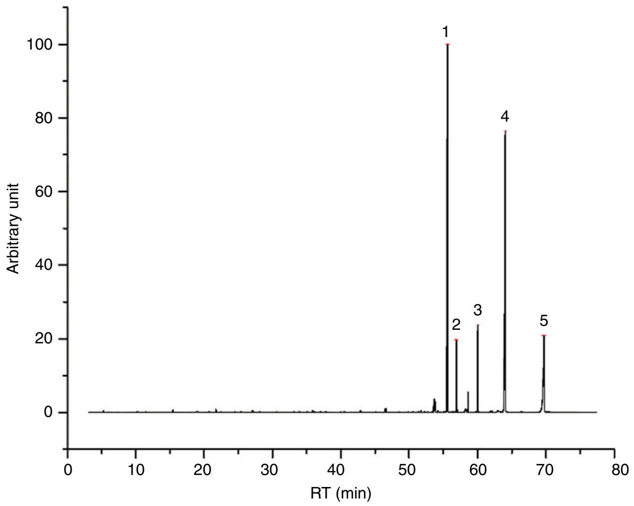

Fig. 5 – I53 chromatogram – (1) 1-methylethyl laurate, (2) 2-ethylhexyl octanoate, (3) 2-ethylhexyl decanoate, (4) 2-ethylhexyl laurate and (5) 2-ethylhexyl myristate.

acid, above all), which may derive from a hybrid formulation between paraffins and one or more esters, as minor components (see Table 6 for details). I2 thermal behavior show one principal weight loss connected to an endothermic event, according to paraffins behavior.

Emissions of ester based inks (34/55), as well as their thermal behavior, depend on the nature of the ester or of the ester mixture.

I33 (Fig. 4) is a good example for 2-ethylhexyl esters mixtures, as main vehicle fraction. In its chromatogram, 2-ethylhexyl laurate, myristate, decanoate and octanoate represent the main peaks, underlining evaporation phenomena. Together, we found few aldehydes and alcohols (especially 2-ethyl-1-hexanol) from the decomposition of these esters, potentially correlated to the exothermic event seen in DTA graph.

I53 emissions are characterized mainly by 1-methylethyl laurate (Fig. 5), mixed with a 2-ethylhexyl esters mix, as made clear by the presence of 2-ethylhexyl laurate, decanoate, myristate and octanoate. Compared to I33, the principal weight loss is linked more to the first endothermic event, rather than to the second exothermic one, according to the behavior of 1-methylethyl laurate. Some decomposition products are observed as well (aldehydes, 2-ethyl-1-hexanol, etc.), together with a quite small portion of glycols. Tables 7 and 8 report the entire results of I33 and I53 analyses.

Emissions of glycol + ester based inks (4/55) show the characteristic emissions of both the fractions. Glycols produce evaporation products (as described for I23). Emissions from the ester fraction depend on the nature of the ester itself. In I50 (Fig. 6), for example, we found 2-ethylhexyl laurate as major component, with aldehydes and 2-ethyl-1-hexanol, coming from the decomposition of a portion of the ester part. The thermal behavior of this ink in DTA is described by an endothermic

Table 7 – Identified compounds in I33 emissions.

RT (min)	Compound
15.464	Pentanal
21.732	Hexanal
27.080	Heptanal
33.649	2-Propanol, 1-(2-methoxy-1-methylethoxy)-
33.895	Octanal
34.493	2-Propanol, 1-(2-methoxypropoxy)-
35.849	1-Hexanol, 2-ethyl-
36.100	1-Hexanol, 2-ethyl-
39.947	Nonanal
42.850	2-Nonenal, (E)-
45.085	Decanal
48.600	Undecanal
53.522	Pentadecane
55.249	?
56.897	Octanoic acid, 2-ethylhexyl ester
58.343	1-Decanol, 2-hexyl-
60.030	Decanoic acid, 2-ethylhexyl ester
62.140	?
64.118	Lauric acid, 2-ethylhexyl ester
66.474	1-Eicosene
69.768	Myristic acid, 2-ethylhexyl ester

Table 8 – Identified compounds in I53 emissions.

RT (min)	Compound
15.473	Pentanal
21.746	Hexanal
27.064	Heptanal
35.823	1-Hexanol, 2-ethyl-
42.854	2-Nonenal
46.470	Tripropylene glycol
46.610	Tripropylene glycol
51.723	*n*-Capric acid isopropyl ester
53.536	Tripropylene glycol *n*-butyl ether
53.626	Tripropylene glycol *n*-butyl ether
53.712	Tripropylene glycol *n*-butyl ether
53.802	Tripropylene glycol *n*-butyl ether
55.590	Lauric acid, 1-methylethyl ester
55.635	Lauric acid, 1-methylethyl ester
56.911	Octanoic acid, 2-ethylhexyl ester
57.117	X
58.643	Isopropyl Myristate
60.045	Decanoic acid, 2-ethylhexyl ester
64.057	Lauric acid, 2-ethylhexyl ester
69.707	Myristic acid, 2-ethylhexyl ester

event, at temperatures comparable to TPnB evaporation, followed by an exothermic phenomenon, probably linked to the decomposition of the ester. Two weight losses are clearly visible and linkable to these two events, one for each. Table 9 displays all the recognized molecules.

The pattern of emissions of paraffin + ester inks (2/55) is well represented by I24 (Fig. 7). Its emissions (Table 10) are characterized by evaporation products from the paraffin (linear and branched alkanes), aldehydes and 2-ethylhexanol from the decomposition of part of the ester fraction, 2-ethylhexyl decanoate, laurate and myristate, and isopropyl palmitate from the evaporation of part of the ester mix. As for I50, DTA proposes two events, the first endothermic, the second exothermic, but it seems that just one major weight loss is present and principally connected to the endothermic

Table 9 – Identified compounds in I50 emissions.

RT (min)	Compound
15.463	Pentanal
21.749	Hexanal
22.457	1-Octene
27.127	Heptanal
28.176	Heptanal
33.197	2-Octanone
35.853	1-Hexanol, 2-ethyl
42.893	2-Nonenal
46.488	Tripropylene glycol
46.628	Tripropylene glycol
49.109	?
51.484	2,4-Undecadienal-
53.392	Tripropylene glycol *n*-butyl ether
53.658	Tripropylene glycol *n*-butyl ether
53.758	Tripropylene glycol *n*-butyl ether
53.849	Tripropylene glycol *n*-butyl ether
60.040	Decanoic acid, 2-ethylhexyl ester
64.147	Lauric acid, 2-ethylhexyl ester
69.680	Myristic acid, 2-ethylhexyl ester

Table 10 – Identified compounds in I24 emission.

RT (min)	Compound
10.241	Butanal
15.459	Pentanal
21.726	Hexanal
27.090	Heptanal
32.318	4-Heptanone, 2,6-dimethyl-
35.839	1-Hexanol, 2-ethyl-
51.262	Dodecanal
53.522	Pentadecane
53.612	Tripropylene glycol *n*-butyl ether?
53.702	Tripropylene glycol *n*-butyl ether?
53.793	Tripropylene glycol *n*-butyl ether?
54.621	Pentadecane, 4-methyl-
54.722	Pentadecane, 2-methyl-
54.862	Pentadecane, 3-methyl-
55.239	?
55.340	Hexadecane
56.213	Pentadecane, 2,6,10-trimethyl-
56.314	Hexadecane, 4-methyl-
56.399	Hexadecane, 2-methyl-
56.535	Hexadecane, 3-methyl-
56.896	Octanoic acid, 2-ethylhexyl ester
56.957	Heptadecane
57.132	Pentadecane, 2,6,10,14-tetramethyl-
57.851	Heptadecane, 4-methyl-
57.931	Heptadecane, 2-methyl-
58.067	Heptadecane, 3-methyl-
58.483	Octadecane
58.624	Isopropyl myristate
58.740	Pentadecane, 2,6,10,14-tetramethyl-
60.015	Decanoic acid, 2-ethylhexyl ester
60.106	Nonadecane
62.155	Isopropyl palmitate
63.988	Lauric acid, 2-ethylhexyl ester
66.474	Cyclohexadecane, 1,2-diethyl-
69.638	Myristic acid, 2-ethylhexyl ester

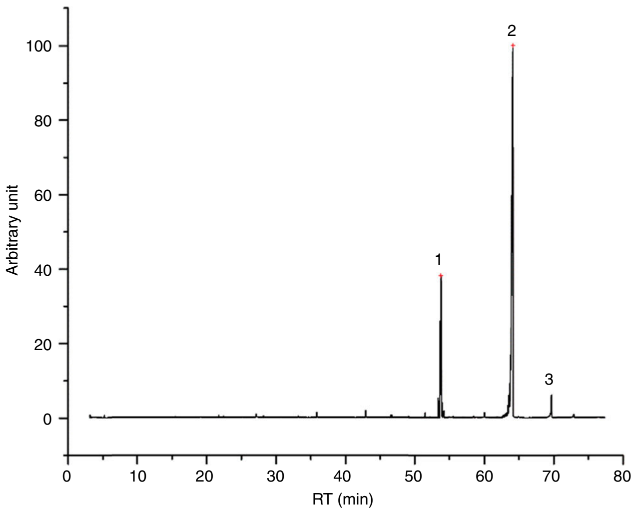

Fig. 6 – I50 chromatogram – (1) tripropylene glycol *n*-butyl ether, (2) 2-ethylhexyl laurate and (3) 2-ethylhexyl myristate.

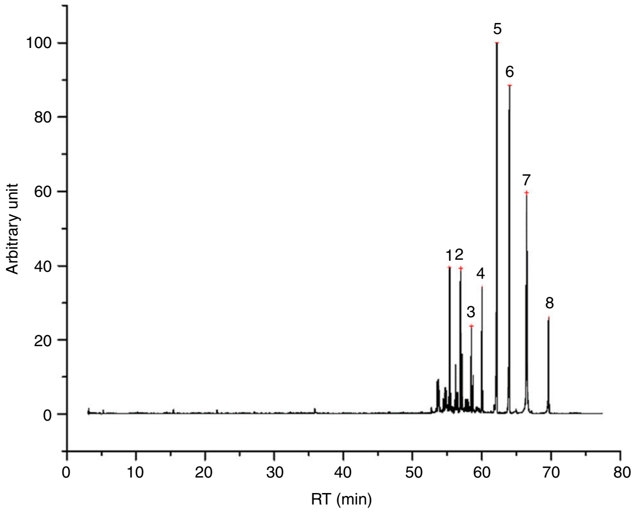

Fig. 7 – I24 chromatogram – (1) hexadecane, (2) heptadecane, (3) octadecane, (4) 2-ethylhexyl decanoate, (5) isopropyl palmitate, (6) 2-ethylhexyl ester laurate, (7) 1,2-diethyl-cyclohexadecane and (8) 2-ethylhexyl myristate.

reaction. This could be the sum of paraffin and ester evaporation, the products of which then go through a combustion process.

Conclusions

To resume the obtained results, the most utilized vehicles for the production of ceramic inks can be divided in 3 groups, considering their thermal behaviors and, consequently, their emissions:

- Vehicles with evaporating behavior: paraffins and TPM.
- Vehicles with hybrid behavior: TPnB, 2-EHL (or, more precisely, 1-MEL), EHC.
- Vehicles with decomposing behavior: 2-EHS and CCT.

Among the decomposition products, esters release aldehydes (from butanal to tridecanal), ketones (from 2-pentanone to 2-tridecanone), carboxylic acids (from octanoic to hexadecanoic acid), alcohols (most of all 2-ethyl-1-hexanol), alkanes, lactones (found only in CCT), fatty acids esters.

TPnB can decompose into some aldehydes and, above all, minor ethers and 2-ethyl-4-methyl-1,3-dioxolane.

Inks, whether they are based on mixtures or nearly pure vehicles, follow the thermal behavior and the emissions pattern of their single components. The set of commercial inks analyzed underline how fatty acids esters are quite common, used as single vehicle or in mixtures with glycols or paraffins. Considering that every analyzed sample of ester-based vehicle seems to meet with a total exothermic reaction or, at least, with a partial one, decomposition products of esters characterize the majority of inks samples.

Moreover, it seems that EHC is the most common ester used for ester based inks. Its hybrid thermal behavior leads to the presence of both evaporation (2-ethylhexyl laurate, myristate, decanoate and octanoate) and decomposition products (aldehydes – pentanal, hexanal, octanal, nonanal – 2-ethyl-1-hexanol).

These results should clearly be implemented by experimentations at real chimneys or by firing in combustion ovens, because the different nature of the industrial ovens could change somehow the actual behavior of inks.

Anyway, assuming the configuration of industrial ceramic kilns, the huge air flow causes the removal of decomposition and evaporation products, conducting them to chimneys, where they can exit into the atmosphere, if they are not able to react completely or to be retained by specific systems.

Among the emission products, the specialized legislation on ceramic industry in Italy puts attention to quantification of aldehydes, so future steps of this study could imply their quantification.

This first characterization is just the initial step to investigate the entire problem. On the basis of these data, we are carrying on comparative studies between emissions of inks alone, collected in laboratory, and emissions of the same inks applied to ceramic tiles, gathered both in laboratory and at a ceramic chimney, to understand the real influence of inks on total emissions.

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