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Identification by GC-MS Analysis of Organics in Manufactured Articles through a D-Optimal Design

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Abstract: Many manufactured articles are made of composite materials often bonded by a phenolic resin. Through a D-optimal design, we optimized a method to characterize phenolic resins after the extraction process by GC-MS analysis. The study was conducted on three different phenolic resins and four manufactured articles with the same inorganic composition and different analyzed binders. Moreover, three cardanol resins that differ in their production systems were analyzed to see if there were differences between them. Through Soxhlet extraction with dichloromethane or acetone, it is possible to differentiate the raw materials through characteristic compounds and to identify them in the manufactured articles.

Keywords: phenolic resin; cardanol resin; characterization; GC-MS; D-optimal design

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1. Introduction

In the material world, phenolic resins are widely used substances: a century after their development, a volume of 6 million tons/year is used as resin systems [1].

Phenolic resins are obtained by a reaction between phenol and formaldehyde, and they are divided into novolacs and resols based on the different molar ratio between the reagents and the type of catalysis, either acid (e.g., oxalic acid, sulfuric acid, phosphoric acid) or basic, respectively [2]. Moreover, novolac resins are thermally cured with a cross-linking agent, such as paraformaldehyde, trioxane and cyclic formals, and hexamethylenetetramine [3]. Additionally, in manufactured articles where phenolic resins are used, various types of them have been utilized: not only non-modified, but also oil-, cashew-, cresol-, rubber-, silicon-, and boron–phosphorous-modified resins [3–7].

A particular phenolic resin is the cardanol resin. Cardanol is a component of cashew nutshell liquid (CNSL), extracted from the cashew nutshell. This molecule is a phenol with an alkylic chain of 15 carbon atoms with up to three unsaturations in the meta position. Thanks to the alkyl groups, the solubility, dielectric and gas permeability properties of a polymer improve [8] and they provide more flexibility to the resin structure and better impact properties [9]. There are different ways to produce cardanol resin; one of them is the reaction between cardanol and an aldehyde under acid catalysis [10]. Formaldehyde [8,11–14] and furfural [15] are examples of aldehydes that are used for the reaction. Depending on the type of reaction, the type of reagents [8,16], their molar ratio [17] and other parameters such as temperature [18], different characteristics are obtained.

Phenolic resins and their modifications are used in different applications: wood composite adhesives, foam, mineral wool insulation binders, laminates, composites, abrasives, friction, photoresists, foundry and more [3]. Usually, these manufactured articles are made of composite materials.

Despite the complexity of these materials, it could be possible to identify the inorganic components by different techniques such as Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), or X-ray Fluorescence (XRF) [19–21]. Moreover, spectroscopic analyses (e.g., Raman and FTIR spectroscopy) could also be used to characterize inorganic components [22].

On the contrary, regarding organic components, it is not possible to carry out a complete characterization using these techniques, as only the spectroscopies could give some general information. The major problems come from binders; the most used are phenolic resins that, once cross-linked, are difficult to recognize and characterize. This is a limit for companies, which results in them being "blind" to the organic binder of their composite materials. For this reason, finding a characterization method for organic components, more specifically for phenolic resin, is essential for the quality control sector of the industries, since these analyses could give information about the quality and the properties of their articles.

In this study, a valid method of qualitative characterization of thermo-curing phenolic resin present in some different manufactured objects is described. The objects are produced by binding inorganic materials with phenolic resins cross-linked at high temperatures. The resins were dissolved in different solvents and the extracts were characterized by GC-MS analyses. Through comparison with analyses of raw materials, it is possible to determine whether there is a specific compound in the matrix. To accomplish this, a Design of Experiments (DOE) study was carried out to understand which was the best extractive method. This model was only used on raw materials without treatment, since they should have the highest content of compounds, to choose which analysis parameters to adopt for all samples. This study can make an important contribution to organic characterization in this type of material for companies, as there is currently no similar work in the literature.

2. Materials and Methods

2.1. Chemicals and Solvents

The solvents used in this study were of analytical grade. Dichloromethane (CAS 75-09-2) was obtained from: Titolchimica (Pontecchio Polesine (RO), Italy), HPLC grade; Merck KGaA (Darmstadt, Germany), HPLC grade; Sigma-Aldrich (St. Louis, MO, USA), ≥99.8%. Acetone (CAS 67-64-1) was obtained from Sigma-Aldrich (St. Louis, MO, USA), ≥99.8%. Heptane (CAS 142-82-5) was obtained from Sigma-Aldrich (St. Louis, MO, USA), ≥99%.

2.2. Samples

In this study, both raw materials and manufactured articles were analyzed, but due to the privacy of the cooperating company, we cannot report either the origin of the former or the specific nature of the latter. Raw materials were analyzed as is, cured (except for cardanol resin, which comes from the manufacturer already cured), and conditioned after curing to simulate the manufacturing process of these articles. In Table 1, the analyzed samples are reported.

Between the different cardanol resins analyzed, there are some differences in the production process. Samples C and D are made by the same company with cashew nutshell liquid, paraformaldehyde and furfuraldehyde; the difference lies in the different origin of the materials. Sample E is made like the previous two but using boric acid as a curing agent. Sample F is produced using cashew nutshell liquid and hexamethylenetetramine as a curing agent.

2.3. Chemometric Model

For this study, an experimental design was applied to choose the two best extraction methods. A D-optimal design [23] was used to understand how many analyses were necessary to obtain the best result, to simplify the development of the analytical method, and to reduce the number of experiments to be performed. The D-optimal design strategy

was also chosen because of its particular features allowing its further tuning even during the development of the methodology; indeed, it was applied after performing some experiments, which were later included in the model, too.

Table 1. List of samples analyzed.

Sample	Type	Note
A	Phenolic resin (raw material)	As is
A1	Phenolic resin (raw material)	Cured
A2	Phenolic resin (raw material)	Conditioned
B	Silicone modified resin (raw material)	As is
B1	Silicone modified resin (raw material)	Cured
C	Cardanol resin (raw material)	As is
C1	Cardanol resin (raw material)	Conditioned
D	Cardanol resin (raw material)	As is
E	Cardanol resin (raw material)	As is
F	Cardanol resin (raw material)	As is
W	Manufactured article	With A, C
X	Manufactured article	With A
Y	Manufactured article	With C
Z	Manufactured article	With B, C

The model was built considering five independent variables (factors): type of extraction, three kinds of solvent (where every type was considered as a single factor), and time of GC-MS analysis. The extraction was performed involving Soxhlet or sonication processes; the solvent was selected from acetone, dichloromethane, and heptane, while the time of the GC-MS analysis could vary from 24 up to 30 min. Therefore, two levels were selected for every independent variable.

The use of a traditional, full-factorial design would have required, at least, the preparation of 32 experiments, without involving any replicates.

In the present work, the use of D-optimal design allowed the preparation of 11 experiments. In actuality, 7 experiments were performed as screening; then, a further 4 experiments were performed after the D-optimal evaluation of the available factors and levels.

The starting model was linear with interaction:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3$$

where b_i are the model coefficients and X_i are the independent variables. Subsequently, an X matrix of dimensions ($n \times p$) was built, where n is the number of experiments and p the number of coefficients in the model.

With Fedorov's algorithm [24,25], the best experiments were determined between the thirty-two calculated by the Chemometric Agile Tool software [26] (see Table S1). Then, the number of experiments to be prepared was determined through the logarithm of the normalized determinant M:

$$M = \frac{\det(X'X)}{np}$$

Since the normalized determinant weighted the information according to the experimental effort required to obtain a robust DOE model, the best results were obtained at high log(M) values.

2.4. Samples Preparation

Powder samples were used for the extractions. From manufactured articles, the powder was retrieved by column drill.

Curing was carried out in an oven at 140 °C for 10 min; the conditioning was carried out at 220 °C for 30 min. After treatment, the sample was ground by a mill.

2.4.1. Soxhlet Extraction

Extraction was carried out using 3.0 g of the sample with 200 mL of solvent. Extraction was performed for 18 h in an oil bath at 95 °C; finally, it was dried and solubilized in 1 mL of solvent.

2.4.2. Sonication Extraction

Sonication extraction was carried out on 0.5 g of the sample with 5 mL of solvent in a test tube for 40 min. After centrifugation (15 min, 1096× *g*), 1 mL of supernatant was recovered for the analysis.

2.5. GC-MS Analyses

An Agilent gas chromatograph-mass spectrometer 5973 inert Mass Selective Detector equipped with an Hp-5 methyl-siloxane column (30 m × 250 µm × 0.25 µm film thickness; Zebron GC column, Phenomenex, Torrance, CA, USA) was used. Samples were injected in a splitless mode; helium was used as a gas carrier with a flow rate of 1.1 mL min^{-1}. The following oven temperature program was applied:

For the 24 min analysis: held at 50 °C for 2.0 min, increased to 300 °C at a rate of 15 °C min^{-1} and maintained at 300 °C for 5.33 min.
For the 30 min analysis: held at 60 °C for 2.0 min, increased to 300 °C at a rate of 15 °C min^{-1} and maintained at 300 °C for 12 min.
The EI energy was 70 eV and it was held at 230 °C. A solvent delay of 4 min was set. Detection was carried out in full scan mode covering a mass range (m/z) of 29–600 amu.

Compound Identification

The identification of compounds present in the samples was performed by comparing the mass spectra of the unknown molecules with those in the Nist05. Identification of the compound was valid when the confidence rating of mass spectra comparison was superior or equal to 90.

3. Results

3.1. Chemometric Model

The results of Fedorov's algorithm are reported in Figure 1.

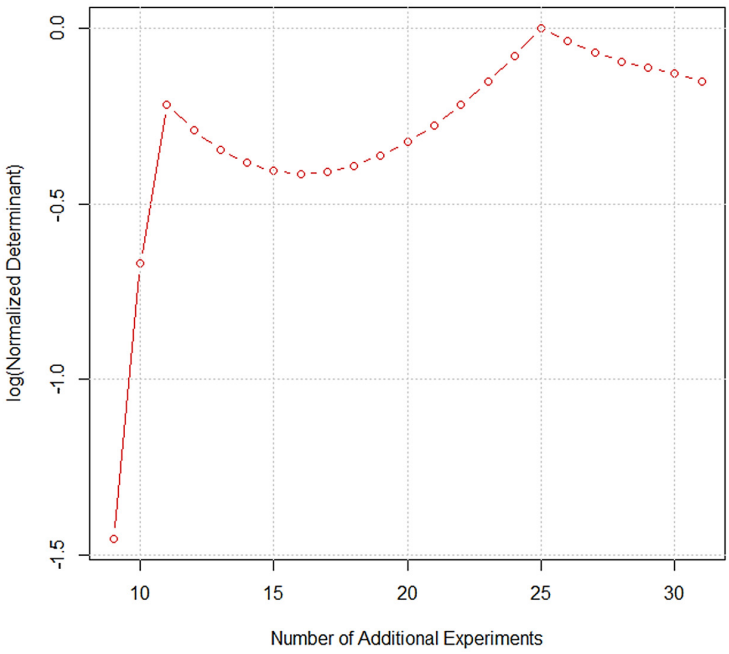

Figure 1. Log(M) as a function of the number of experiments.

The plot describes the behavior of the logarithm of M as a function of the number of experiments. From the plot, it can be observed that the log(M) value increases up to 11 experiments; then, after a brief decrease, it continues increasing to a value of 25 experiments. Since the performance of 25 experiments would have been too expensive and time-consuming, a good trade-off involved the preparation of 11 experiments.

Since 7 experiments had already been performed, only 4 new experiments were carried out by choosing among the 32 calculated by the D-optimal design. Table 2 reports the experiments performed.

Table 2. Experimental parameters: where for acetone, dichloromethane, heptane +1 is yes, −1 is no; for extraction +1 is sonication process, −1 is Soxhlet process; for time of GC analysis +1 is 30 min, −1 is 24 min.

	# Experiment	Acetone	Dichloromethane	Heptane	Extraction	Time GC Analysis
Before DOE	1	+1	−1	−1	−1	−1
	2	−1	+1	−1	−1	−1
	3	−1	+1	−1	−1	+1
	4	+1	−1	−1	−1	+1
	5	−1	−1	+1	+1	+1
	6	−1	+1	−1	+1	+1
	7	+1	−1	−1	+1	+1
After DOE	8	−1	+1	−1	+1	−1
	9	−1	−1	+1	+1	−1
	10	+1	+1	−1	+1	−1
	11	+1	+1	+1	+1	+1

The results from the D-optimal design were then evaluated, as a screening approach, to estimate the significance of the experimental parameters under exam. The dependent response (Y) under exam was the number of identified compounds in the analyzed samples (A, B and C). As reported in Figure 2, only the dichloromethane and heptane parameters were significant.

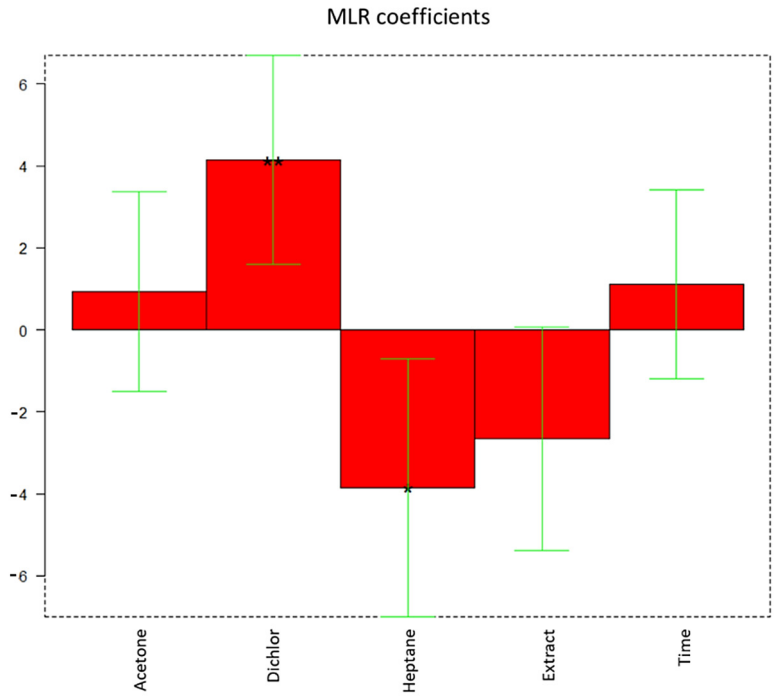

Figure 2. Significance of the experimental parameters in terms of MLR coefficients from the D-optimal analysis. The * and ** symbols indicate the significant *p*-values lower than 0.05 and 0.01, respectively.

In particular, the use of dichloromethane as a solvent favored the extraction and identification of a higher number of compounds, and the absence of heptane within the analytical procedure was preferred. The use of Soxhlet or sonication extraction was not significant, but Soxhlet extraction, when employed, was preferred to sonication since it provided a slightly higher number of identified compounds.

The use of acetone and the time of GC-MS analysis were both non-significant parameters. Therefore, the faster GC-MS analytical conditions were used to diminish the time of analysis. Moreover, since the use of acetone provided a higher (but not significant) number of identified compounds, its combination with Soxhlet extraction was evaluated too, in parallel with the one involving dichloromethane.

3.2. GC-MS Analysis

All the identified compounds of each sample are reported in the Supplementary Materials (Tables S2–S14), indicating in which experiment each molecule was found. The tables below (Tables 3 and 4) show only the most characteristic compounds of each sample.

Table 3. Characteristic compounds in samples A–F.

Sample	Compound	CAS	t_R (min)	# ID
A	phenol	108-95-2	5.2	1
	2-hydroxybenzaldehyde	90-02-8	6.0	2
	4-methylphenol	106-44-5	6.3	3
	benzoic acid	65-85-0	7.5	4
	1,3,5,7-tetrazatricyclo[3.3.1.13,7]decane	100-97-0	8.2	5
	2-[(2-hydroxyphenyl)methyl]phenol	2467-02-9	14.0	6
	2-[(4-hydroxyphenyl)methyl]phenol	2467-03-0	14.3	7
	4-[(4-hydroxyphenyl)methyl]phenol	620-92-8	14.6	8
	2-[(2-hydroxy-5-methylphenyl)methyl]-4-methylphenol	3236-63-3	15.0	9
A1	phenol	108-95-2	5.1	1
	2-[(2-hydroxyphenyl)methyl]phenol	2467-02-9	14.0	6
	2-[(4-hydroxyphenyl)methyl]phenol	2467-03-0	14.3	7
	4-[(4-hydroxyphenyl)methyl]phenol	620-92-8	14.6	8
A2	-	-	-	-
B	phenol	108-95-2	5.1	1
	2-hydroxybenzaldehyde	90-02-8	5.9	2
	4-methylphenol	106-44-5	6.2	3
	2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane	541-02-6	6.7	10
	1,3,5,7-tetrazatricyclo[3.3.1.13,7]decane	100-97-0	8.1	5
	benzene-1,2-dio	120-80-9	8.3	11
	4-hydroxybenzaldehyde	123-08-0	9.1	12
	2,2,4,4,6,6,8,8,10,10,12,12,14,14-tetradecamethyl-1,3,5,7,9,11,13-heptaoxa-2,4,6,8,10,12,14-heptasilacyclotetradecane	107-50-6	9.9	13
	phenylmethoxymethylbenzene	103-50-4	11.4	14
	2,2,4,4,6,6,8,8,10,10,12,12,14,14,16,16,18,18,20,20-icosamethyl-1,3,5,7,9,11,13,15,17,19-decaoxa-2,4,6,8,10,12,14,16,18,20-decasilacycloicosane	18772-36-6	13.4	15
	2-[(2-hydroxyphenyl)methyl]phenol	2467-02-9	13.9	6
	2-[(4-hydroxyphenyl)methyl]phenol	2467-03-0	14.2	7
	4-[(4-hydroxyphenyl)methyl]phenol	620-92-8	14.6	8
B1	phenol	108-95-2	5.1	1
	2-hydroxybenzaldehyde	90-02-8	5.9	2
	1,3,5,7-tetrazatricyclo[3.3.1.13,7]decane	100-97-0	8.0	5
	2,2,4,4,6,6,8,8,10,10,12,12,14,14-tetradecamethyl-1,3,5,7,9,11,13-heptaoxa-2,4,6,8,10,12,14-heptasilacyclotetradecane	107-50-6	9.9	13
	2-[(4-hydroxyphenyl)methyl]phenol	2467-03-0	14.1	7
	4-[(4-hydroxyphenyl)methyl]phenol	620-92-8	14.6	8
	2,2,4,4,6,6,8,8,10,10,12,12,14,14,16,16-hexadecamethyl-1,3,5,7,9,11,13,15-octaoxa-2,4,6,8,10,12,14,16-octasilacyclohexadecane	556-68-3	16.6	16

Table 3. *Cont.*

Sample	Compound	CAS	t_R (min)	# ID
C	phenol	108-95-2	5.1	1
	hexadecan-1-ol	36653-82-4	13.2	17
	2-methylpropyl tetradecanoate	25263-97-2	13.6	18
	(E)-hexadec-9-enoic acid	2091-29-4	13.6	19
	(Z)-hexadec-11-enoic acid	2416-20-8	13.7	20
	(E)-octadec-9-enal	5090-41-5	13.8	21
	hexadecanoic acid	57-10-3	13.8	22
	2-methylpropyl hexadecanoate	110-34-9	14.9	23
	octadec-9-enoic acid	2027-47-6	15.1	24
	octadecanoic acid	57-11-4	15.2	25
	1-methyl-4-(4-methylphenyl)sulfonylbenzene	599-66-6	15.4	26
	hexadecyl (Z)-octadec-9-enoate	22393-86-8	16.0	27
	butyl (Z)-octadec-9-enoate	142-77-8	16.0	28
	2-methylpropyl octadecanoate	646-13-9	16.1	29
	1-methoxy-3-pentadecylbenzene	15071-57-5	16.6	30
	3-pentadecylphenol	501-24-6	17.0	31
C1	2-methylpropyl hexadecanoate	110-34-9	14.9	32
	1-methyl-4-(4-methylphenyl)sulfonylbenzene	599-66-6	15.3	26
	butyl (Z)-octadec-9-enoate	142-77-8	16.0	28
	2-methylpropyl octadecanoate	646-13-9	16.1	29
	3-pentadecylphenol	501-24-6	16.9	31
D	1-(furan-2-yl)ethanone	1192-62-7	4.9	33
	benzaldehyde	100-52-7	5.5	34
	(E)-3-(furan-2-yl)prop-2-enal	623-30-3	7.3	35
	butyl furan-2-carboxylate	583-33-5	8.2	36
	3H-2-benzofuran-1-one	87-41-2	9.7	37
	2-dodecoxyethanol	4536-30-5	12.1	38
	(Z)-pentadec-11-enal	-	12.5	39
	2-methylpropyl dodecanoate	37811-72-6	12.8	40
	tetradecanoic acid	544-63-8	12.9	41
	pentadecanoic acid	1002-84-2	13.6	42
	(Z)-hexadec-11-enoic acid	2416-20-8	13.7	20
	hexadecanoic acid	57-10-3	13.8	43
	methyl hexadecanoate	112-39-0	14.1	44
	octadec-9-enoic acid	2027-47-6	15.6	24
	octadecanoic acid	57-11-4	15.7	25
	1-methyl-4-(4-methylphenyl)sulfonylbenzene	599-66-6	15.9	26
	1-methoxy-3-pentadecylbenzene	15071-57-5	16.6	30
	3-pentadecylphenol	501-24-6	17.0	31
E	5-methylfuran-2-carbaldehyde	620-02-0	4.9	45
	benzoic acid	65-85-0	7.9	4
	(E)-4-(furan-2-yl)but-3-en-2-one	41438-24-8	8.1	46
	3H-2-benzofuran-1-one	87-41-2	9.7	37
	decanoic acid	334-48-5	9.8	47
	dodecanoic acid	143-07-7	11.4	48
	tetradecanoic acid	544-63-8	13.0	41
	methyl (E)-hexadec-11-enoate	55000-42-5	13.3	49
	propan-2-yl tetradecanoate	110-27-0	13.4	50
	methyl hexadecanoate	112-39-0	13.5	44
	pentadecanoic acid	1002-84-2	13.6	42
	(Z)-hexadec-11-enoic acid	2416-20-8	13.7	20
	propan-2-yl hexadecanoate	142-91-6	14.1	51
	heptadecanoic acid	506-12-7	15.1	52
	octadecanoic acid	57-11-4	15.1	25
	methyl (E)-octadec-9-enoate	1937-62-8	15.2	53
	octadec-9-enoic acid	2027-47-6	15.7	24
	3-pentadecylphenol	501-24-6	16.9	31
F	benzaldehyde	100-52-7	4.9	34
	octanoic acid	124-07-2	7.3	54
	hexadecanenitrile	629-79-8	13.3	55
	pentadecanenitrile	18300-91-9	13.4	56
	(Z)-hexadec-11-enoic acid	2416-20-8	13.7	20
	(E)-hexadec-9-enoic acid	2091-29-4	13.7	19
	hexadecanoic acid	57-10-3	13.8	43
	3-[(2-methyl-5-nitrophenyl)iminomethyl]phenol	-	13.9	57

Table 3. *Cont.*

Sample	Compound	CAS	t_R (min)	# ID
F	heptadecanoic acid	506-12-7	14.4	52
	octadec-1-ene	112-88-9	14.5	58
	(Z)-octadec-9-enenitrile	112-91-4	14.6	59
	octadecanenitrile	638-65-3	14.7	60
	(E)-octadec-9-enoic acid	112-79-8	15.0	24
	(Z)-octadec-6-enoic acid	593-39-5	15.1	61
	octadecanoic acid	57-11-4	15.2	25
	hexadecanamide	629-54-9	15.3	62
	(Z)-octadec-9-enamide	301-02-0	16.2	63
	3-pentadecylphenol	501-24-6	17.0	31

Table 4. Characteristic compounds in samples W–Z.

Sample	Compound	CAS	Raw Material	t_R (min)	# ID
W	phenol	108-95-2	A–C	5.1	1
	2-hydroxybenzaldehyde	90-02-8	A	6.0	2
	4-hydroxybenzaldehyde	123-08-0	A	9.2	12
	2-[(4-hydroxyphenyl)methyl]phenol	2467-03-0	A	14.2	7
	4-[(4-hydroxyphenyl)methyl]phenol	620-92-8	A	14.6	8
	2-methylpropyl hexadecanoate	110-34-9	C	14.9	23
	1-methyl-4-(4-methylphenyl)sulfonylbenzene	599-66-6	C	15.4	26
	3-pentadecylphenol	501-24-6	C	17.0	31
X	phenol	108-95-2	A	5.1	1
	2-hydroxybenzaldehyde	90-02-8	A	6.0	2
	benzoic acid	65-85-0	A	7.5	4
	4-hydroxybenzaldehyde	123-08-0	A	9.2	12
	2-[(4-hydroxyphenyl)methyl]phenol	2467-03-0	A	14.2	7
	4-[(4-hydroxyphenyl)methyl]phenol	620-92-8	A	14.6	8
Y	Phenol	108-95-2	C	5.1	1
	hexadecan-1-ol	36653-82-4	C	13.2	17
Z	2-hydroxybenzaldehyde	90-02-8	B	6.0	2
	4-hydroxybenzaldehyde	123-08-0	B	9.2	12
	phenylmethoxymethylbenzene	103-50-4	B	11.5	14
	hexadecan-1-ol	36653-82-4	C	11.8	17
	2-[(4-hydroxyphenyl)methyl]phenol	2467-03-0	B	14.2	7
	4-[(4-hydroxyphenyl)methyl]phenol	620-92-8	B	14.6	8

For manufactured articles' samples (from W to Z), only compounds that are found in raw materials are reported and, in the tables, the attribution of each molecule to the raw material is also shown.

3.2.1. Samples A to F

In Table 3, the characteristic identified compounds of samples A to F and their derivatives are reported.

In the Supplementary Materials (Figure S1), the chromatogram of sample A with the parameters of Experiment 2 (Soxhlet extraction with dichloromethane and time of analysis of 24 min) is reported. From sample A, we can note that the extraction did not completely break the links in the polymer, but only the molecules that were not cross-linked were recovered and analyzed, and as a matter of fact, in sample A1, and more so in A2, there is a minor number of molecules. In sample A2, we did not find characteristic compounds due to both the high curing rate and the fact that at high temperatures, some compounds may have evaporated. In these samples, compounds with phenolic groups or substituted bisphenols were found, confirming the phenolic nature of the resin. Moreover, hexamethylenetetramine and benzoic acid were found, which are a curing agent and cross-linking catalyst, respectively. It is interesting to note that these molecules were not present

in A1 and A2, since such molecules are completely consumed during the curing process. These data immediately give us an indication of whether the resin has been cross-linked or still has some non-cured parts. Thus, the presence of some specific molecules (i.e., hexamethylenetetramine) can be considered the first quality indicator of an incomplete curing process.

Figures S2 and S3 in the Supplementary Materials represent the chromatograms of samples B and B1, respectively, carried out with the parameters of Experiments 8 (sonication extraction with dichloromethane and time of analysis of 24 min) and 2 (Soxhlet extraction with dichloromethane and time of analysis of 24 min), respectively. Compounds that were present in sample B were like sample A: phenolic and bisphenolic molecules. This is a confirmation that they are both phenolic resins. Moreover, sample B contained some siloxane molecules that are characteristic of its modification. Not many siloxanes had a good match within the library, but in the chromatograms, there were many peaks with the characteristic mass spectrum of these compounds. This extraction method enabled us to recognize a specific modification of a resin and therefore to distinguish between two different phenolic resins. This aspect is of fundamental importance in the quality control sector of a product. Moreover, many molecules, including hexamethylenetetramine, were still present in sample B1, which may be an indicator of less curing than in sample A1. Sample B was not analyzed after conditioning, since A2, with the same heat treatment, did not show the presence of compounds.

The chromatogram of sample C with the parameters of Experiment 2 (Soxhlet extraction with dichloromethane and time of analysis of 24 min) is reported in the Supplementary Materials (Figure S4). Although it is a phenolic resin, sample C is completely different from previous ones. Here, indeed, there were several phenyl compounds, but also many molecules, alcohols, and esters, with long alkylic chains absent in samples A and B. The latter may come from cardanol oil; moreover, oleic acid ((Z)-octadec-9-enoic acid) is a characteristic compound of oily substances.

Sample D has the same composition as sample C; they are made by the same company, but they are produced with different starting materials. Compared to sample C, in D, different furan molecules were found; this may be an indicator of a lower degree of curing as the extraction collects the non-cross-linked portion. Moreover, in samples C and D, di-p-tolyl sulfone (1-methyl-4-(4-methylphenyl)sulfonylbenzene) was identified that was not in the other cardanol resins studied: this compound is characteristic of this company and can be seen as a marker of their production process.

The cardanol resin of Sample E used boric acid as a curing agent; there were no molecules with boron, but there were many with furan groups. As in sample D, this may be an indication of low curing.

In sample F, characteristic compounds of cardanol resin, such as carboxylic acids attributable to cardanol oil, were identified. In addition, there were many molecules with nitrogen, both nitriles and amides, that may come from reactions between compounds present in cardanol oil and hexamethylenetetramine, which is used in the preparation of this material. Also in this case, the presence of some specific molecules is an indication of an incomplete curing process.

Comparing samples from C to F, we can recognize different chemicals present in samples and thus attribute them to a specific production process and even to a specific supplier. Both of these aspects are fundamental for a good quality control of an industrial product.

Having analyzed and characterized the raw materials, it is now interesting to see if these are recognizable within the manufactured article.

3.2.2. Samples W to Z

In Table 4, characteristic molecules of samples W to Z are shown with comparisons to raw materials.

Sample W contained A and C as organic materials. Through the extraction, many characteristic molecules attributable to these were found. Phenol cannot be used as a marker

of a specific material, because in the analysis of raw materials, it was found in both, while bisphenols (i.e., 4-[(4-hydroxyphenyl)methyl]phenol; 2-[(4-hydroxyphenyl)methyl]phenol) and the hydroxybenzaldheydes (i.e., 2-hydroxybenzaldehyde; 4-hydroxybenzaldehyde) were present only in the phenolic resin extraction. In the same way, di-p-tolyl sulfone and 3-pentadecylphenol are characteristic of cardanol resin, but while the first is specific to a company, the second is characteristic of this material, but not for a specific brand. Other molecules were found, but they were not attributable to the raw material studied until now. Figure 3 shows the chromatogram of DCM extraction of sample W.

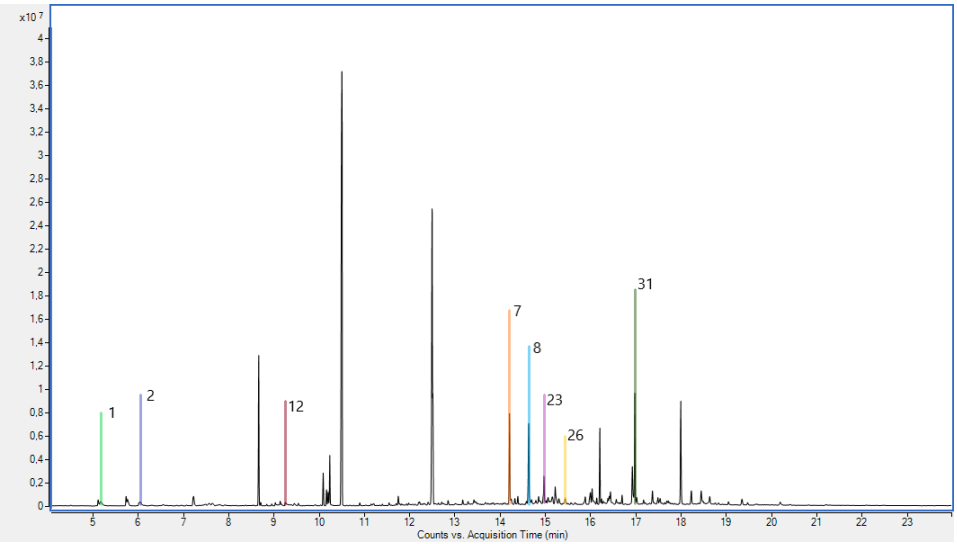

Figure 3. Chromatogram of DCM extraction of sample W with # ID.

Sample X contained only unmodified phenolic resin, justifying the results of the analysis. In fact, hydroxybenzaldheydes (i.e., 2-hydroxybenzaldehyde; 4-hydroxybenzaldehyde) and bisphenols (i.e., 2-[(4-hydroxyphenyl)methyl]phenol; 4-[(4-hydroxyphenyl)methyl]phenol) that are characteristic of this type of resin were extracted. In this case, molecules particular to cardanol resin were not present; thus, the absence of this component was confirmed. The chromatogram of DCM extraction of sample X is reported in Figure 4.

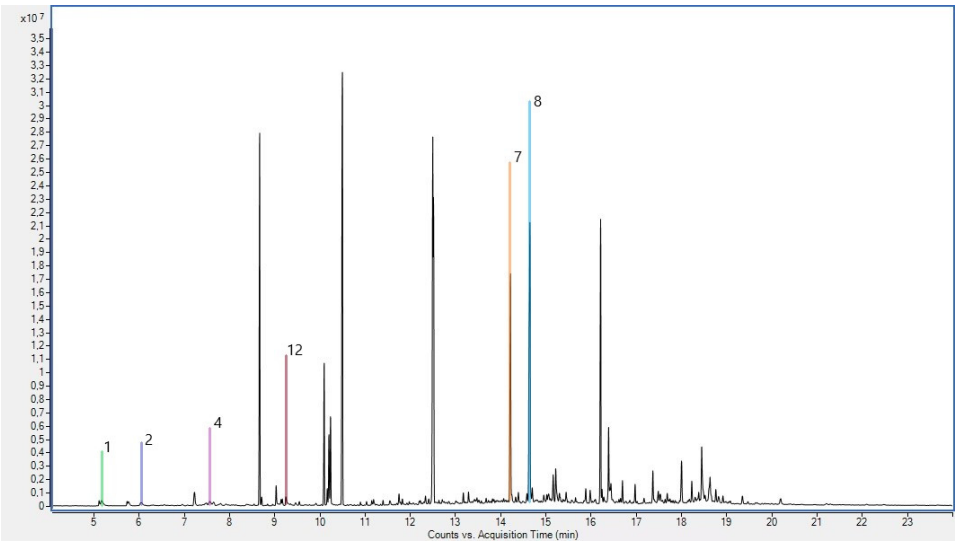

Figure 4. Chromatogram of DCM extraction of sample X with # ID.

In sample Y, there was only cardanol resin. Not many compounds were found, but 1-hexadecanol is characteristic of this type of resin. The results of samples Y and X are

perfect examples of possible quality control analysis. If a compound is produced without an organic component, it can be easily recognized with this analytical method. Figure 5 shows the chromatogram of DCM extraction of sample Y.

In sample Z, different molecules characteristic of phenolic resin, such as bisphenols (i.e., 2-[(4-hydroxyphenyl)methyl]phenol; 4-[(4-hydroxyphenyl)methyl]phenol), were found. In addition, there were many compounds that were not identified by the library, but whose mass spectra were attributable to silanes or siloxanes. Since these peaks were not present in other samples and since the only change made between the different pads was in the resin, it can be deduced that these signals derive from the resin used, thus distinguishing the one silicone modified from the other one. The chromatogram of DCM extraction of sample Z is reported in Figure 6.

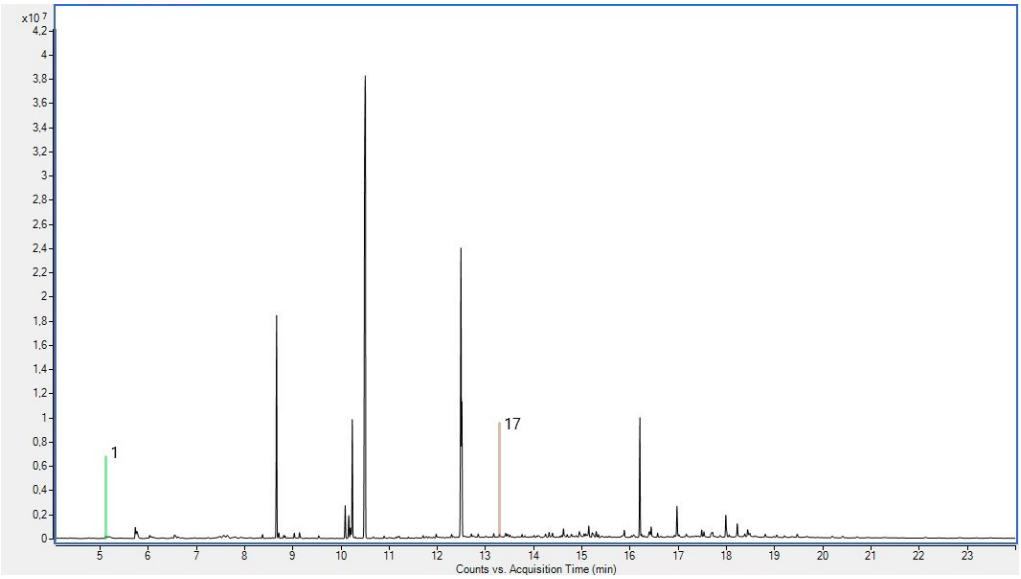

Figure 5. Chromatogram of DCM extraction of sample Y with # ID.

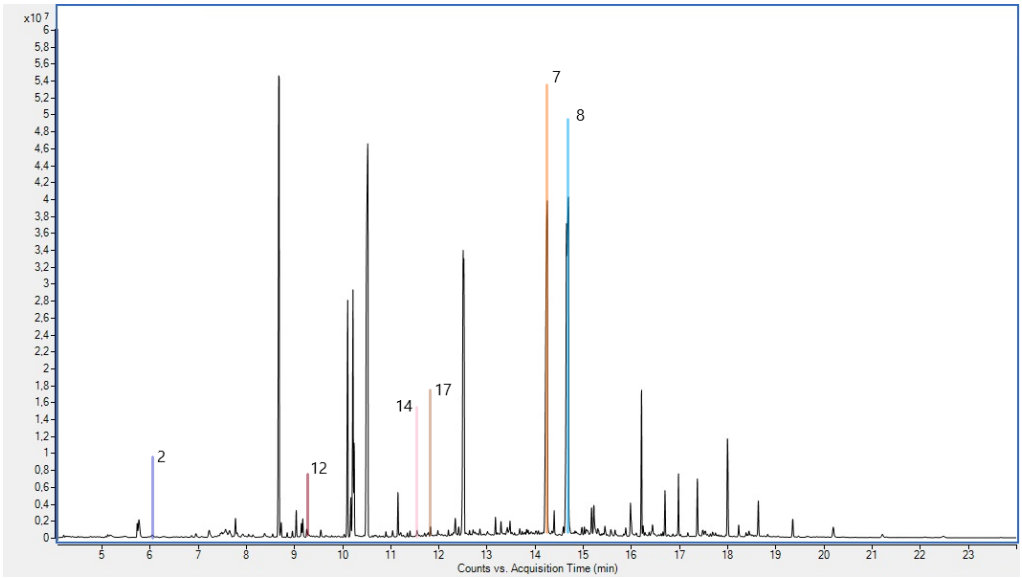

Figure 6. Chromatogram of DCM extraction of sample Z with # ID.

4. Conclusions

The use of GC-MS analysis with an experimental design has brought improvements in the knowledge of the organics present in manufactured articles. Through a D-optimal

design, a model with five independent variables (type of extraction, three kinds of solvent and time of GC-MS analysis) has been applied for the analyses of raw materials. After that, the two best extraction methods were identified (extraction with dichloromethane and acetone, both with Soxhlet apparatus) and they were used to analyze all the samples. Regarding the time of GC-MS analysis, there was no difference between the two methods, so the faster one was used.

The analyses of raw materials show that it is possible to differentiate between different materials, not only by nature (phenolic resins vs. cardanol resins), but also by different manufacturers and production systems, thanks to the characteristic compounds of each one (between cardanol resins). Bisphenols are characteristic of phenolic resins, while carboxylic acids with long alkylic chains are representative of cardanol resins.

Through the same analysis for manufactured articles, it can be possible to identify the raw materials by finding the same characteristic molecules of starting substances. This can be extremely useful for companies to control their own finished products and to study the organics in other manufacturers' articles.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app12147320/s1, Figure S1: Chromatogram of sample A with the parameters of Experiment 2. Figure S2: Chromatogram of sample B with the parameters of Experiment 8. Figure S3: Chromatogram of sample B1 with the parameters of Experiment 2. Figure S4: Chromatogram of sample C with the parameters of Experiment 2. Table S1: Experiments calculated by Chemometric Agile Tool software; where for acetone, dichloromethane, heptane +1 is yes, −1 is no; for extraction +1 is sonication process, −1 Soxhlet process; for time of GC analysis +1 is 30 min, −1 is 24 min. Table S2 Compounds in sample A. Table S3: Compounds in sample A1. Table S4: Compounds in sample B. Table S5: Compounds in sample B1. Table S6: Compounds in sample C. Table S7: Compounds in sample C1. Table S8: Compounds in sample D. Table S9: Compounds in sample E. Table S10: Compounds in sample F. Table S11: Compounds in sample W. Table S12: Compounds in sample X. Table S13: Compounds in sample Y.

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