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Exploratory study on the possibility to link gasoline samples sharing a common source after alteration by evaporation or combustion

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Abstract :

The source inference of ignitable liquids in forensic science is still a challenging and ongoing research area. In real case applications, specimens of different natures, which may have been exposed to fire or not, may have to be compared. These comparisons are difficult since specimens may have been altered by evaporation, combustion or both. Plus, the extent of the alteration is often difficult to evaluate. Most studies concerning source inference of ignitable liquids worked on neat samples or samples altered by evaporation. However, there is a lack of studies comparing the influence of evaporation and combustion within a source inference framework. In this study, the same collection of gasoline samples was altered by both evaporation under a nitrogen stream and combustion of the gasoline adsorbed on a matrix. The possibility to link gasoline samples sharing a common source was then explored using an adaptive untargeted chemometrics workflow from feature detection to feature selection. This data treatment approach was successfully applied to the data and it was shown that the possibility to link samples with a common source was not compromised despite evaporation or combustion for degrees of alteration from 0% to 99%.

Keywords : source inference ; gasoline comparison ; evaporation ; combustion ; chemometrics

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Abstract

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1. Introduction

Arsonist identification is a challenging task due to the lack of physical evidence. The golden standards for human identification such as DNA traces and fingermarks are usually destroyed in the fire or they are not even looked for since they are assumed to be destroyed. This paradox raises
5 the need to find an alternative to link the arsonist to the crime scene. The inference of traces of ignitable liquids to a potential source could be used as a suitable alternative [1]. In fact, at the Central Laboratory of the Paris Prefecture of Police, it is not rare that the investigators ask to evaluate the relationship between traces of ignitable liquids detected on site and some potential source brought forward by the investigation. In a source inference perspective, specimens of
10 different natures may have to be compared in order to evaluate the possibility of them sharing

a common source. The comparison could be made between two ignitable liquids altered or not, between a liquid and traces of an ignitable liquid adsorbed on a support or even between two traces of ignitable liquids adsorbed on possibly different supports. Moreover, all these objects could have been exposed to fire or not, which complicates even more the comparison. In the end, the information resulting from these comparisons could be used as court evidence or as intelligence within the investigation [2].

Ignitable liquids stored in containers not hermetically sealed or exposed to fire can undergo alteration by evaporation and combustion. The general alteration trend results in a faster loss of the more volatile compounds compared with the heavier ones [3], which therefore gain importance throughout the alteration. Also, interfering products and microbial degradation can hinder the interpretation process [4]. In fact, fire debris analysts analyze altered ignitable liquids more frequently than neat ones. Whereas standard practice based on the visual interpretation of chromatograms for ignitable liquid residue identification is well suited for neat ignitable liquids, the task is more challenging for altered ones [5, 6]. This is also the case if the objective is to evaluate the possibility of two ignitable liquids, altered or not, sharing a common source.

Studies investigating the effect of evaporation on the feasibility of linking ignitable liquids sharing a common source have mainly concerned samples altered at room temperature or under a nitrogen stream. In order to formulate exclusions of common source, Mann used peak-to-peak ratios [7, 8] between the most volatile compounds of gasoline. Comparisons were hampered by evaporation because the compounds used for discrimination were the first to disappear after alteration and so could not be used for comparison purposes when dealing with high alteration degrees. Dolan *et al.* [9, 10] used area ratios between pairs of compounds eluting consecutively to formulate exclusions of common source for gasoline samples evaporated from 0 to 75% by volume. Sandercock and Du Pasquier [11] used the less volatile compounds of gasoline (polycyclic aromatics) to link samples sharing a common source after evaporation between 0 and 90% by weight loss. Results showed that independently of the evaporation degree it was possible to link altered gasoline samples based on naphthalenic compounds through the use of Principal Components Analysis (PCA) followed by Linear Discriminant Analysis (LDA). Vergeer *et al.* [12] compared evaporated gasoline residues up to 75% by weight loss using peak area ratios minimizing the intravariability for gasoline samples sharing a common source and maximizing intervariability for those not sharing a common source. Evaluation of the strength of evidence was conducted using three likelihood ratio methods for the source inference of gasoline samples in order to provide a transition from categorical statements to numerical values. Likelihood

ratio methods following chemometric classification tools were also used by Sigman and Williams
45 [13] to infer the presence or absence of ignitable liquid residues. Besson [14] successfully used
area ratios between compounds eluting consecutively from toluene to the C2-natphthalenes in
order to link altered gasoline samples that were evaporated between 0 and 90% by weight loss.
Differentiation of the altered samples was performed using both Hierarchical Cluster Analysis
(HCA) and similarity measurements between pairs of samples followed by Receiver Operating
50 Characteristics (ROC) analysis.

The aforementioned studies on gasoline comparisons showed that it was possible to link
gasoline samples sharing a common source irrespective of the evaporation degree up to 90%.
It must be noted, however, that the physico-chemical phenomena involved in the alteration of
ignitable liquids in real case specimens may involve not only evaporation but also combustion.
55 Moreover, the temperature at which the alteration occurs is expected to have an influence on
the chemical profile of the ignitable liquids residues. Birks et al. [15] pointed out three factors
known to influence the relative distribution of weathered ignitable liquids in order of magnitude
of the effect: percent of weathering > temperature > nitrogen gas. While the nitrogen gas
has a negligible effect, the higher the temperature at which the alteration occurs, the higher
60 the effect on the distribution of the chemical profile. The authors suggested that weathering at
high temperatures increased the evaporation of less volatile compounds compared with the more
volatile ones, as an explanation for the lack of weathering in some casework specimens. The
effect of high temperatures combined with the effect of entrapment caused by the nature of the
matrix on which the ignitable liquid residues are adsorbed may explain the weathered profile
65 of some specimens. It is then expected that these factors may also interfere in the process of
gasoline comparison within a source inference framework.

Research in the field of fire debris analysis has been mainly focused on the detection of ig-
nitable liquid residues and the identification of their class according to the ASTM E1618. Several
chemometrics classification tools such as LDA and Soft Independent Modeling of Class Analogy
70 (SIMCA) have been used to detect and identify ignitable liquids using data such as the Total
Ion Spectrum (TIS) [16, 17, 18, 19] and related approaches such as Extracted Ion Spectra (EIS)
[20] and the Segmented TIS [21]. In fact, these classification tools can only be used when the
groups to be discriminated contain several individuals, which is not the case in an individual-
ization framework since each group contains only one unique individual. Moreover, even if the
75 use of TIS-related approaches may avoid the need for the retention time alignment, chemical
interpretation of the data is very challenging since information contained in the chromatographic

domain is totally or partially eliminated.

In this study, we evaluated the influence of the alteration mode by evaporation or combustion on the possibility to link ignitable liquids sharing a common source. Gasoline being the ignitable liquid the most often detected in fire debris at the Central Laboratory of the Paris Prefecture of Police (France), the present study focused on this liquid. Gasoline samples of different qualities and brands were altered by evaporation and combustion to four degrees of alteration by weight loss (0, 50, 90 and 99%). Evaporation of the liquids was done under a nitrogen stream and combustion was done using a cone calorimeter after pouring the liquids onto purified sea sand as support matrix. Samples were then prepared by passive headspace extraction onto Tenax TA tubes before Automated Thermo Desorption (ATD-) GC-MS analysis in both the evaporation and the combustion experiments. The data acquisition protocol, parameters and treatment were those described in [22]. This exploratory study applied the steps of the chemometric workflow from the detection of features to the calculation and selection of the most discriminant ratios between pairs of feature areas. This chemometric approach being based on the calculation of similarity measurements between pairs of samples sharing a common source or not, it was deemed adapted to tackle the question of the source inference of altered gasoline samples. ROC analysis was used to evaluate the separation between pairs of samples sharing a common source from those which did not. This separation was optimized using the Area Under the ROC curve (AUROC) to select discriminant ratios. In this work, following the definition of Besson [14], each unique gasoline sample was an aliquot of what is considered here to be a source, i.e. the unquantifiable volume of gasoline contained in a given gas station tank at a given time. To the best of the authors' knowledge, this is the first study exploring the possibility to link gasoline samples sharing a common source after alteration by evaporation or combustion.

2. Material and methods

2.1. Gasoline samples

Twelve gasoline samples representing 5 brands and 4 qualities (unleaded 95, unleaded 98, unleaded 95-E10 and superethanol E85) were purchased the same day in October 2016 in 4 gas stations located in Paris (France) and the immediate surrounding area. The samples were collected at the gas pumps in 1 L Duran protect laboratory bottles (GL 45) before being closed with caps equipped with a PTFE membrane and stored in a spark-free refrigerator at 5°C. A Quality Control (QC) sample was created by mixing several reference gasoline samples.

2.2. Sample alteration and extraction

2.2.1. Evaporation

110 The alteration by evaporation of the gasoline samples was performed under a constant nitrogen stream until the desired weight loss was reached (0, 50, 90 and 99%). The experimental procedure involved the following steps: a 2 mL vial was tared with its cap on a precision balance; 1.5 mL of gasoline were added to the vial; the vial containing the gasoline with its cap was weighed; the targeted mass for a given alteration degree was calculated; the weight loss was
115 monitored throughout the evaporation until the targeted weight was reached. Each of the twelve gasoline samples was evaporated in triplicate for each alteration degree: $3 \times 0\%$, $3 \times 50\%$, $3 \times 90\%$ and $3 \times 99\%$ for a total of 144 samples, whose extraction procedure was undertaken as follows.

Both evaporated (50, 90 and 99%) and unaltered (0%) gasoline samples were prepared by
120 passive headspace extraction onto stainless steel ATD prepacked Tenax TA tubes with PTFE caps (PerkinElmer). In a 660 mL glass jar, about 3 g of sea sand purified by acid and calcined for analysis (Merck Millipore) were added and placed against the jar's inner wall. A Tenax TA tube was hung opposite the sand before adding 10 μL of gasoline onto the sand and sealing the jar with its lid. Extraction was carried out for 1 hour in an oven at 90°C and the system was
125 cooled down for 30 minutes at room temperature before retrieving the tube and sealing it with its caps.

2.2.2. Combustion

The alteration of the gasoline samples by combustion was performed on a Fire Testing Technology Cone Calorimeter until the desired weight loss was attained. Each of the twelve gasoline
130 samples was prepared in triplicate at 50, 90 and 99% for a total of 108 combustions. Unaltered samples (0%) were prepared in the evaporation procedure. The combustion experiments were performed using the following procedure: in a Pyrex Petri dish (9.4 cm inner diameter and 2 cm height) about 25 g of sea sand purified by acid and calcined for analysis were uniformly distributed; a tare of the sand plus the Petri dish was performed on the cone calorimeter balance; 15 mL of gasoline were deposited in the center of the Petri dish and ignited with a long
135 stem lighter; the weight loss was followed on the digital screen of the cone calorimeter until the targeted weight loss was reached; combustion was stopped by oxygen starvation by placing an insulating rockwool square over the Petri dish; the content of the Petri dish was recovered in a 660 mL glass jar immediately after oxygen starvation.

140 Gasoline samples altered by combustion underwent the same passive headspace thermal ex-
traction procedure as the evaporated samples. The main difference was that after combustion,
the remaining gasoline was adsorbed on the sand and it was not possible to sample a known quan-
tity of liquid. Thus, the samples had to be prepared by weighing a part of the sand containing
gasoline, or all of it (0.1 g for 50%, 2.5 g for 90% and 25 g for 99%).

145 2.2.3. *Experimental design*

This section explains the choices made concerning the experimental design presented above.
First, the choice of the sea sand to include matrix effects in the alteration experiments must be
detailed. In real case specimens, the matrix composition influences the extraction of ignitable
liquids from fire debris. It is true that sea sand does not constitute one of the most commonly
150 encountered matrices. However, the chosen sea sand has some interesting properties. It has the
advantage of not producing any interfering products since it was calcined for analysis. Plus, the
mass loss on ignition at 900 °C is not more than 0.05%, which is important since it ensures that
the mass loss observed during the combustions was mostly due to the combustion of the gasoline
and not to the degradation of the matrix. This point is decisive since alterations of samples were
155 done up to 99% by weight loss and the balance precision of the cone calorimeter was only 0.1
g. Activated charcoal was an alternative matrix considered since commonly encountered charred
debris have similar adsorptive properties [23], e.g. wood (charcoal). Nevertheless, commercial
activated charcoal can exhibit a loss on drying up to 10% corresponding to the mass loss of water
and any other volatile compound, which is not a desirable property given the aimed alteration of
160 up to 99% and the precision of the cone calorimeter. For the reasons mentioned in this paragraph
and because it would be difficult to select a matrix representative of all the matrices frequently
encountered in fire debris, sea sand was deemed adapted to take account for matrix effects in
this exploratory study.

Secondly, the reader may have noticed that the alteration procedures for evaporation and
165 combustion are quite different, which may raise some questions regarding the comparability of
the results. In fact, the combustion experiments were performed by including the sea sand as
a matrix since the beginning of the alteration. As for the evaporation experiments, those were
performed in vials without sand and the liquids were then poured on the matrix for extraction
only after evaporation. In order to be consistent, the evaporation experiments should have been
170 performed by including the matrix effect from the beginning. The reason for not doing so was
linked to practicality since evaporations including a matrix are time-consuming and cumbersome.

Moreover, it is not impossible in practice that the fire debris analyst may have to compare a liquid present in a container, which was not evaporated after adsorption on a matrix, with ignitable liquid residues adsorbed on a burned matrix. In that sense, even though the procedures of alteration of the samples by evaporation and combustion are fundamentally different, they produce samples that may have to be compared in three real casework situations: (1) the comparison of two ignitable liquids evaporated or not; (2) the comparison of an ignitable liquid evaporated or not with traces of an ignitable liquid adsorbed on a matrix; (3) the comparison of two traces of ignitable liquids adsorbed on a matrix. Furthermore, from the perspective of common source inference between traces of ignitable liquids, different protocols for sample preparation cannot be considered an unsurpassable issue since in practice the creation of the specimens is not controlled. In fact, the specimens being compared may have been created under drastically different conditions and it is of utmost interest to evaluate the possibility to link ignitable liquids sharing a common source, which were altered under different conditions.

2.2.4. QCs and blanks

A total of 124 QC samples and 110 procedural blanks were prepared in parallel with the (un-)altered gasoline samples. Their preparation was identical to the evaporation experiments, except that for the blanks no gasoline was added before extraction. The number of QC and blank samples used is due to the fact that all the samples at the various alteration modes and degrees were analyzed over a time period of several months and not in a row. During this time period, QCs and blanks were analyzed frequently to follow the analytical response in order to select features stable over time, as will be presented in the chemometric methodology.

2.3. Sample analysis

The analysis of the samples adsorbed onto the Tenax TA tubes was performed by ATD on a PerkinElmer TurboMatrix 650 apparatus followed by a PerkinElmer Clarus 680 Gas Chromatograph (GC) coupled to a PerkinElmer Clarus SQ 8 T Mass Spectrometer (MS). Data acquisition was done in full-scan mode (30-450 amu) on a simple quadrupole after separation on a Restek Rxi-1MS Crossbond 100% dimethylsiloxane (60m x 250 μ m x 0.5 μ m) GC column. All the ATD-GC-MS acquisition parameters used in this study were those given in [22]. A total of 252 samples were analyzed after alteration by evaporation and combustion (36 samples at 0%, plus 72 samples for each alteration degree at 50, 90 and 99% for both evaporation and combustion).

2.4. Data preprocessing

2.4.1. Feature detection

The feature detection was performed with the XCMS package v3.0.0 [24] in R v3.4.0 after
205 conversion of the raw data files into netCDF format. The XCMS parameters used in the feature
detection workflow are shown in Tab. 1. A total of 1,395 features were detected.

Table 1: XCMS parameters used in the feature detection workflow

XCMS method	Parameters
<code>xcmsSet(method = 'matchedFilter')</code>	<code>fwhm=3, step=0.25, steps=3, snthresh=10, mzdif=0.5,</code> <code>max=100, scanrange=NULL</code>
<code>retcor(method = 'obiwarp')</code>	<code>distFunc="cor_opt", profStep=1</code>
<code>group(method = 'density')</code>	<code>bw=3, mzwid=0.25, minfrac=0.50, minsamp=1</code>

2.4.2. Feature filtration

The features detected and integrated with XCMS were filtered. The filtration step consisted
in using the QCs and the blanks to clean the data. All the features detected in the QCs with
210 a median intensity value equal to zero were eliminated. As for the blanks, all the features in
the blanks with a median intensity greater than 1/100 of the overall median intensity in regular
gasoline samples were removed. This filtration step reduced the number of features from 1,395 to
900. For the remaining features, values that were equal to zero or Not-a-Number were replaced
by the corresponding mean value of their respective gasoline replicates. These values represented
215 2.2% of the total number of elements of the matrix with dimensions 252×900 . This relatively
high value was due to the range of alteration degrees considered. In fact, with the increase in the
alteration degree, the lighter compounds were less often detected since they tended to disappear
and the heavier ones were more often detected since there was less competition with the lighter
ones during the passive headspace extraction procedure.

2.4.3. Feature normalization

The features remaining after filtration were normalized using diagnostic ratios calculation
according to Eq. 1 [25]. Ratios were calculated between all possible pairs of features, with
repetition. From the initial 900 features, a total of 809,100 ratios were calculated.

$$Ratio_{A/B} = \frac{A}{A + B} \quad (1)$$

2.4.4. Ratio selection

225 Among the 809,100 calculated ratios, a subset of ratios was selected as the most discriminant to differentiate the 12 gasoline samples, independently of the alteration mode and alteration degree. The first step used the QCs to select the most repeatable ratios over time with a Relative Standard Deviation (RSD) less than or equal to 5%. A total of 169,450 repeatable ratios were retained and the selection of the most discriminant ones was done using a variable selection
230 method based on similarity measurements and the maximization of the AUROC, as described in [26]. The AUROC value is a direct measure of the separation between two populations. If the two populations correspond to similarity measurements between pairs of linked and unlinked samples, the AUROC value is also a measure of the separation between linked and unlinked samples. Furthermore, if linked samples correspond to samples sharing a common source, unlinked samples
235 correspond to samples from different sources. Thus, maximizing the AUROC value between these two populations is equivalent to maximizing the discrimination between samples sharing a common source from those which do not. The similarity measurement used in this work was the Euclidean distance. Calculating the population of linked samples came down to calculating all the possible similarities between pairs of samples, without repetition, from the same source,
240 whereas the population of unlinked samples was calculated between all possible pairs of samples from different sources. The AUROC takes values between 0.5 and 1 included. The closer to 1 the value is, the greater the separation between the two populations. The variable selection method used here selected a subset of ratios maximizing the AUROC value in a forward-like selection step and a backward elimination step. The parameter increment of the variable selection method
245 was fixed at 0.001. The increment corresponds to the minimal increase that a variable must have on the overall AUROC value in order to be selected.

Because it was expected that the range of alteration degrees considered could have an effect on the possibility to link gasoline samples sharing a common source, it was decided to split the problem into three parts of increasing difficulty from 0% (not altered) to 99% (almost completely
250 altered). Hence, the ratio selection was made on samples altered by evaporation and combustion for the alteration degrees : (1) 0% and 50%, (2) 0%, 50% and 90%, (3) 0%, 50%, 90% and 99%. It must be noted that the preparations at 0% correspond only to 36 analyses (the 12 gasoline samples in triplicate) since for 0% there is no mode of alteration to be considered. To summarize, step (1) involved 108 samples: 36 samples at 0%, plus 72 samples at 50% (12 gasolines
255 \times 3 replicates \times 2 modes \times 1 alteration degree); step (2) involved 180 samples: 36 samples at 0%, plus 144 samples at 50% and 90% (12 gasolines \times 3 replicates \times 2 modes \times 2 alteration

degrees); step (3) involved all 252 samples: 36 samples at 0%, plus 216 samples at 50%, 90% and 99% (12 gasolines \times 3 replicates \times 2 modes \times 3 alteration degrees). In each step, all the samples were compared in a pairwise fashion independently of their alteration mode or degree.

260 2.5. Common Components Analysis

Common Components Analysis (CCA) [27] is an exploratory method based on Common Components and Specific Weights Analysis (CCSWA) [28, 29, 30]. In CCSWA, several tables describing the same samples, but not necessarily having the same (number of) variables, are treated in order to iteratively extract Common Components (CCs). Each extracted CC represents
265 a direction of maximum dispersion of the samples in a space common to all the tables. Each table is assigned a 'salience' corresponding to its specific weight in the construction of a given CC. The greater the salience, the greater the contribution of the table to the construction of a given CC. In CCA, each table contains a single variable. The orthogonal CCs extracted by CCA are linear combinations of the original variables, with high saliences for variables with a similar
270 effect on the dispersion of the samples. In CCA, saliences are the square of the loadings and for interpretation purposes, only the loadings will be presented here. More detailed descriptions of CCA and CCSWA can be found in [27, 28, 29, 30, 31].

3. Results and discussion

3.1. Visual comparison

275 Results were first evaluated by a visual comparison of the chromatographic profiles of the gasoline samples altered by evaporation and combustion. Fig. 1 shows a typical gasoline sample (unleaded 95) altered to different degrees and by the two modes. Because of the differences in intensity caused by the increase in the degree of alteration, profiles were normalized to the most intense peak in each chromatogram. These differences are due to the passive headspace
280 extraction procedure and the alteration mode itself. The goal of Fig. 1 is to show the differences in the relative proportions between the (groups of) compounds of gasoline according to the degree and the mode of alteration. Concerning the evaporation experiments, as expected with this phenomenon (Fig. 1, left), the light Volatil Organic Compounds (VOCs) disappeared with the increase of the alteration degree and the heavier VOCs increased.

285 For the combustion experiments, significantly different chromatographic profiles were obtained depending on the alteration mode and degree. On the other hand, combustion profiles (Fig. 1, right) were not altered as much as expected. In fact, for the same alteration degree at

99%, which is almost a complete alteration of the gasoline sample, the C₂-alkylbenzenes (1200-1300 seconds) were still visible in the total ion current of the combustion profile but not in the evaporation profile. This could be explained by the matrix effect that entrapped the ignitable liquid and protected it during the combustion. Moreover, in the case of evaporation, a thermodynamic equilibrium was established between the liquid and its vapor phase. At room temperature, the equilibrium could be shifted towards the formation of the vapors in the headspace of the liquid by sweeping the vapors with a nitrogen stream. In the combustion case, matrix effects were added and there was a double equilibrium: between the ignitable liquid and the matrix, and between the liquid and its vapor phase. In this case, the matrix used was sea sand and it is expected that, depending on the support on which ignitable liquids are adsorbed, matrix effects may change the chromatographic profiles. This question should be addressed in future work.

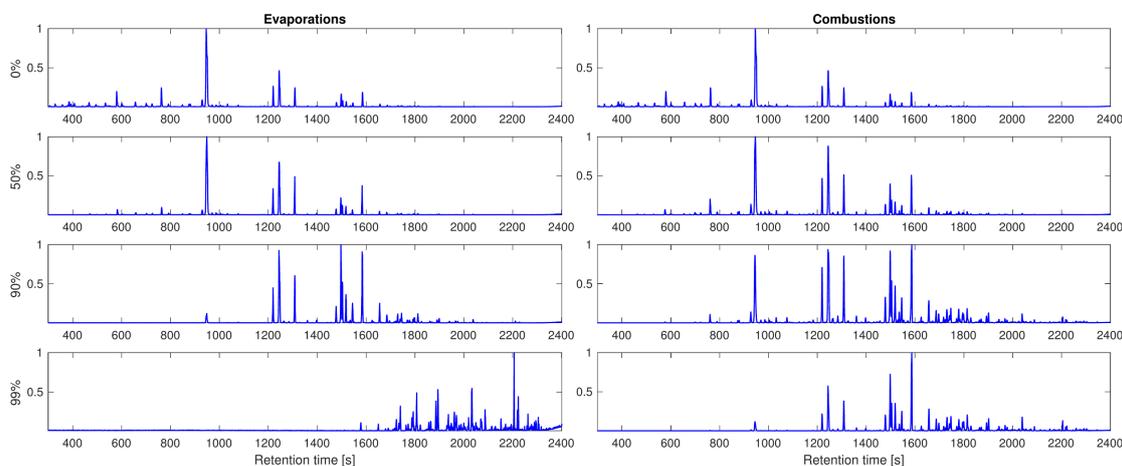


Figure 1: Normalized chromatographic profiles of an unleaded 95 gasoline sample altered by evaporation (left) and combustion (right) at 0, 50, 90 and 99% by weight loss

Given the diversity in the profiles as a function of the alteration mode and degree, visual comparison may be enough to identify an ignitable liquid as gasoline taking into account the evaporation phenomenon but it is not enough within a source inference perspective to link samples. The substantial differences observed between the profiles justify the need to tackle this question with a suitable chemometric approach.

3.2. Ratio selection

Fig. 2 illustrates the evolution of the similarity measurements between samples sharing a common source (linked) and those from different sources (unlinked) when the alteration range

increases. In this figure, the thresholds are only indicative of the point of the ROC curve maximizing both the true positives and true negatives. With the increase of the alteration range, the population of the linked samples becomes wider and it is more difficult to link samples sharing a common source. From a geometrical point of view, the widening of the distribution of the linked samples corresponds to a greater expansion in the multivariate space of the cloud of points sharing a common source. Consequently, clouds of points from different sources get closer together so the distribution of unlinked samples tends to be smaller and this leads to a decrease of the AUROC value.

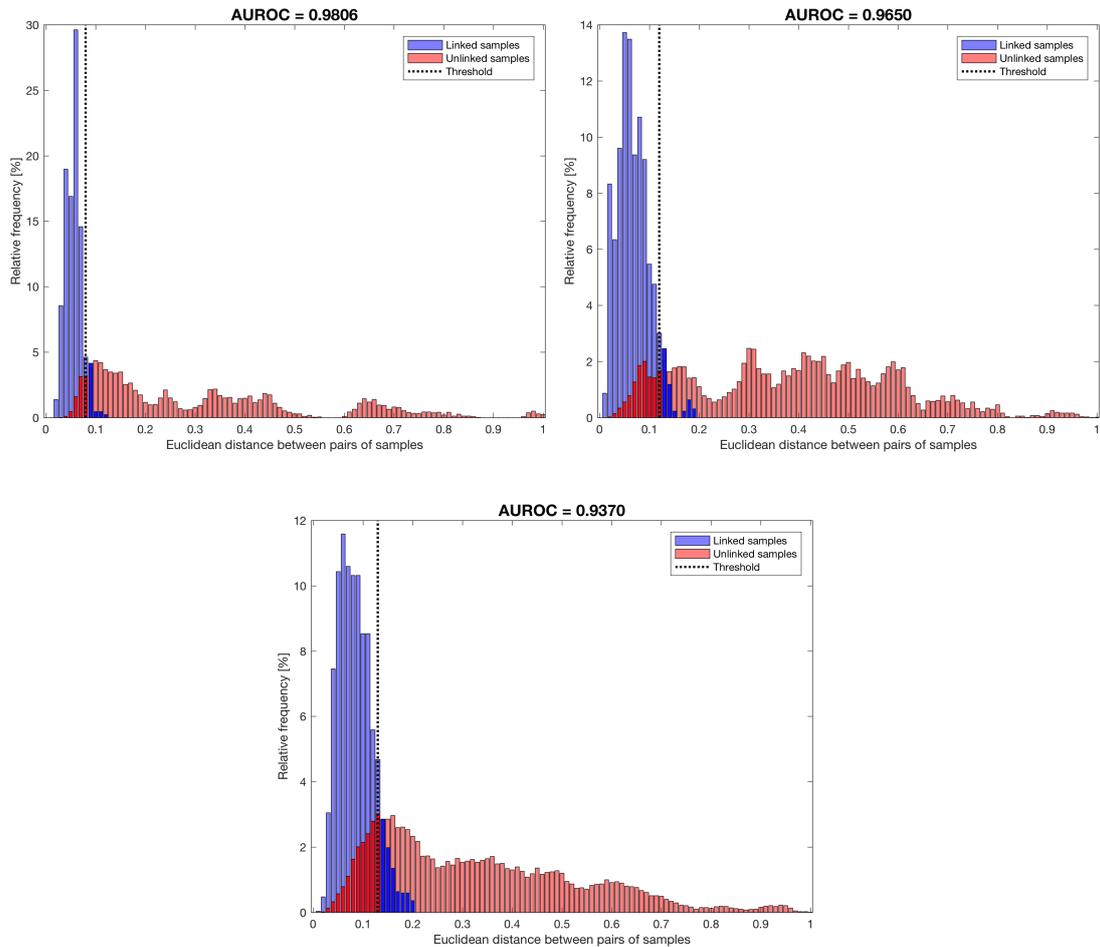


Figure 2: Distributions of the similarities between linked (sharing a common source) and unlinked (from different sources) gasoline samples for both evaporation and combustion experiments with varying alteration ranges : 0% to 50% (top left), 0% to 90% (top right), 0% to 99% (bottom)

315 Tab. 2 shows the numerical results for this. The wider the alteration range considered, the smaller the AUROC value and the bigger the mean distance between pairs of samples sharing a common source. The standard deviation associated with the mean also increases. In terms of the number of ratios selected, the numbers are not significantly different.

Table 2: Results of the variable selection procedure for each of the 3 alteration ranges along with the mean (\bar{x}) and standard deviation (σ_x) of the distribution of linked samples

Alteration ranges	AUROC	Ratios	$\bar{x} \pm \sigma_x$
0% to 50%	0.9806	16	0.0509±0.0162
0% to 90%	0.9650	12	0.0627±0.0322
0% to 99%	0.9370	12	0.0800±0.0344

In order to validate the hypothesis that the widening of the distribution of linked samples was
 320 caused by the increase of the alteration range, the same ratio selection procedure was applied separately to each of the alteration degrees. Better discrimination results were expected for each alteration degree than for a range of alterations. Results are summarized in Tab. 3. The AUROC values for each alteration degree are better than when a range is considered. As for the number of ratios selected, except for the 0% alteration degree, the other degrees selected a similar number
 325 of ratios. This is not surprising because at 0%, the chemical profiles being compared are very similar. However, this is not the case for 50, 90 and 99%, since as discussed in section 3.1, the chemical profiles vary significantly with the degree and mode of alteration. As for the mean and standard deviation values of Tab. 3, they are also smaller for the separate alteration degrees. These results validate the hypothesis that the range of alteration degrees has an influence in the
 330 comparison of the gasoline samples.

Table 3: Results of the variable selection procedure for each of the alteration degrees individually along with the mean (\bar{x}) and standard deviation (σ_x) of the distribution of linked samples

Alteration degrees	AUROC	Ratios	$\bar{x} \pm \sigma_x$
0%	0.9998	4	0.0226±0.0129
50%	0.9896	12	0.0445±0.0138
90%	0.9898	16	0.0511±0.0187
99%	0.9798	12	0.0632±0.0224

The results and discussion above suggest that for an optimal use of this approach, it would

be useful to be able to define approximately the alteration degree (e.g. low, medium, high) of the unknown source. For example, if the traces of unknown source were to be altered around 50%, then it would not be reasonable to include in the variable selection process reference samples that were altered at 90% or more. Prediction performances of the models would be pessimistic representations of reality since possibly substantially different chemical profiles would be compared. Being able to define a narrower alteration range in order to use only relevant reference samples to select ratios and build prediction models to infer the source of traces of ignitable liquid residues is a research topic that may be interesting to tackle in future work.

This section strongly focused on the statistical results obtained from the untargeted chemometric approach used in this study. The discussion showed that from a mathematical point of view, the possibility to link gasoline samples sharing a common source after alteration by evaporation or combustion was not compromised. However, the relevance of the compounds involved in the selected ratios for each of the three ranges of alteration degrees was not evaluated from a chemical point of view. This evaluation is of utmost importance in a forensic context in order to demonstrate that such a data treatment approach is suited to provide answers within the framework of the source inference of ignitable liquids. The next section presents this evaluation.

3.3. Common Components Analysis

In this section, an interpretation of the scores and loadings of CCA is proposed in an attempt to provide chemical interpretation of the compounds involved in the selected ratios. Each of the twelve gasoline samples was identified by a reference number where the information between the first and last letter corresponds to the quality of the gasoline: 95 (unleaded 95), 98 (unleaded 98), E10 (unleaded 95, 10% ethanol), E85 (superethanol). The first letter is a gas station identifier and the last letter refers to the fall season but neither are of concern in this discussion.

Regarding the alteration range between 0% and 50%, Fig. 3 shows the projection of the scores of CC1 and CC2. Fig. 4 presents their respective loadings showing the importance of the selected ratios in Tab. 4 in the construction of the CCs. CC1 and CC2 were retained as the most informative CCs explaining a total of 70% of the variance. In Fig. 3, circles with the same color correspond to the same unique gasoline sample, which was altered by evaporation and combustion to different degrees. As expected, based on the results discussed in section 3.2, circles with the same color are close to each other in this two-dimensional space. This means that independently of the alteration mode (evaporation or combustion) and alteration degree (0% and 50%), samples sharing a common source occupy the same space and may be linked together.

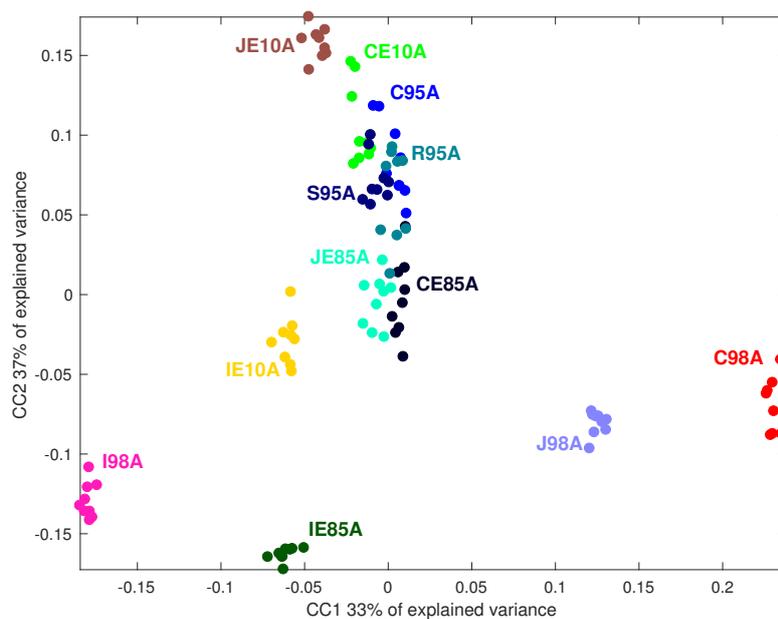


Figure 3: Alteration range between 0% and 50%: scores' projection plot of CC2 versus CC1

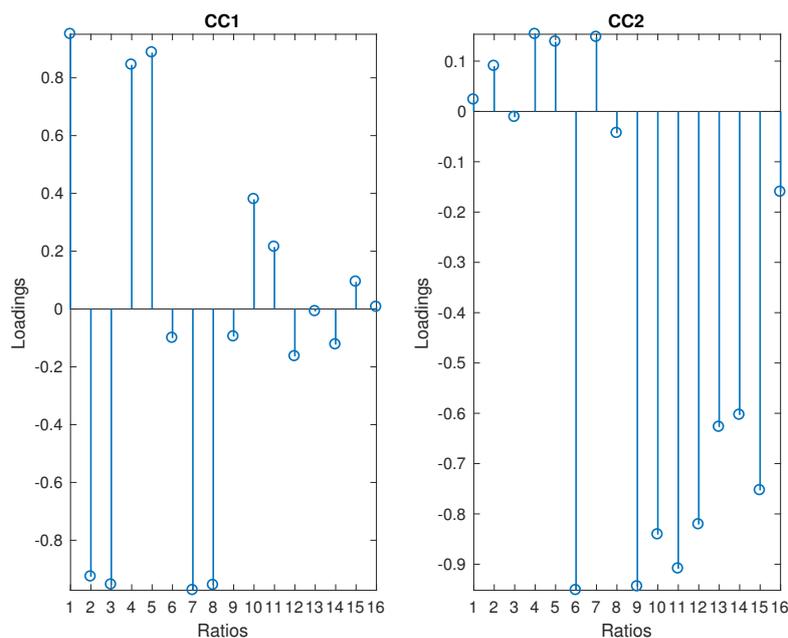


Figure 4: Alteration range between 0% and 50%: loadings of CC1 (left) and CC2 (right)

When looking at the loadings (Fig. 4, left and Tab. 4), the ratios contributing the most (ratios
 365 1, 2, 3, 4, 5, 7 and 8) to the construction of CC1 all have a compound in common, the tetrahy-

drodicyclopentadiene (4H-DCPD). 4H-DCPD is a compound contained in a blend-product called pyrolysis gasoline [32]. Pyrolysis gasoline is a high octane mixture that can be used to boost the octane number of gasoline. CC1 shows a dispersion of gasoline samples where negative scores correspond to higher proportions of 4H-DCPD compared with the associated compound in the ratio and inversely, the positive scores correspond to lower proportions of 4H-DCPD. The dispersion of the samples I98A, J98A and C98A shows that unleaded 98 gasoline samples do not necessarily have an intense 4H-DCPD since other aromatics or oxygenated compounds can be used to boost the octane number. Nevertheless, this reveals an interesting characteristic for individualization since it shows that the intensity of 4H-DCPD can substantially vary in the unleaded 98 gasoline samples. Regarding the other qualities and samples, the variation of 4H-DCPD is not as interesting as previously described but some samples (JE10A, IE10A, IE85A) have a more negative score in the CC1 than the other samples, which represents a greater proportion of 4H-DCPD in the ratios. For the CCs, the loadings of the ratios may be positive or negative. This is due to the role that 4H-DCPD played in the calculation of the ratios, since it was either A or B (Eq. 1). Hence, 4H-DCPD is a characteristic compound for the identification of gasoline [6] but it is also in this case a relevant compound to link gasoline samples sharing a common source, as was already found in a previous study comparing neat gasoline samples [22]. As for CC2, it can be observed that the dispersion of the samples seems to contain information about the octane number. In fact, all unleaded 98 gasoline samples have negative scores on CC2 and their Research Octane Number (RON) is at least 98 initially. All superethanol E85 samples tend to also have negative scores on CC2 and this is not surprising since they are mostly composed of ethanol, which has a high octane number. As for the other gasoline qualities (unleaded 95 and E10), it is expected that they have a lower RON leading to positive scores on CC2. However, it can be observed that sample IE10A has negative scores on CC2, potentially corresponding to a higher octane number than the other unleaded E10 samples. By looking at the identifiers of the samples in the projection of the scores (Fig. 3), it can be seen that the selected ratios have difficulties in differentiating unleaded 95 samples, which may not be as surprising if the projection of the scores on CC2 is related to the octane number of the samples. The relationship between the CC2 and the octane number is explained by the compounds involved in the ratios selected. When looking at the loadings (Fig. 4, right and Tab. 4) of some of the ratios contributing the most (ratios 6, 9, 12, 13 and 14) to the construction of CC2, they involve a high octane compound (aromatic) used as A for the ratio calculation (Eq. 1) with a low octane compound used as B such as (iso)paraffins, a olefin and a naphthene with high numbers of carbon atoms. By looking

at the projection of the scores (Fig. 3) along CC2 and the values of the ratios calculated, it was observed that samples with positive scores on CC2 have higher proportions of low octane compounds compared with the high octane compound they are associated with in the ratios. Inversely, samples with negative scores on CC2 have a higher proportion of the high octane compound, which may represent gasoline samples with higher octane research numbers. As for the ratios n° 10, 11 and 15, they all involve aromatic compounds with high octane numbers. However, similarly to the previous ratios, compounds used as *B* have smaller octane numbers than the compounds used as *A* according to the RON values in [33]. The catalytic reforming process used in refineries to respond to the demand for high-octane gasolines leads to substantial quantities of alkylbenzenes such as 1-methyl-3-ethylbenzene and 1,2,4-trimethylbenzene, which are the most predominant C₃-alkylbenzenes in reformat [34], along with 1-methyl-2-ethylbenzene and these are very often found as *A* compounds in Tab. 4.

The last ratio in Tab. 4 reveals that a compound coming from the bleed of the column is involved. This compound has no relevance for the problem treated but it was selected anyway. This point emphasizes the need to characterize the compounds involved in the ratios because they may have no chemical interest for the problem at hand since they don't enter into the composition of gasoline.

Table 4: Selected ratios for the alteration range between 0% and 50%

Ratio no.	Ion m/z (A)	R _T (A) [s]	Compound A	Ion m/z (B)	R _T (B) [s]	Compound B
1	65	1585	1,2,4-trimethylbenzene	67	1864	4H-DCPD
2	67	1864	4H-DCPD	111.1	1732	1-methyl-3-propyl-benzene
3	95.1	1864	4H-DCPD	98.1	1536	2-methylnonane
4	117.1	1585	1,2,4-trimethylbenzene	108.1	1864	4H-DCPD
5	77	1546	1-methyl-2-ethylbenzene	93.1	1864	4H-DCPD
6	62	946	Toluene	95.1	1097	C8-olefin
7	108.1	1864	4H-DCPD	122.2	1585	1,2,4-trimethylbenzene
8	67	1864	4H-DCPD	98.1	1536	2-methylnonane
9	60	946	Toluene	109.1	1195	C9-naphthene
10	62	1499	1-methyl-3-ethylbenzene	80.1	1980	C11-aromatic
11	117.1	1585	1,2,4-trimethylbenzene	66	1797	1,4-dimethyl,2-ethylbenzene
12	50	1585	1,2,4-trimethylbenzene	113.2	1626	<i>n</i> -decane
13	65	1585	1,2,4-trimethylbenzene	85.1	1873	<i>n</i> -undecane
14	121.1	1519	1,3,5-trimethylbenzene	99.1	1780	C12-isoparaffin
15	52	1585	1,2,4-trimethylbenzene	64	1969	4-methylindane
16	51	946	Toluene	344.1	2663	Column bleed

Concerning the alteration range between 0% and 90%, results of the projection of the scores,

and to some extent the loadings, are similar to those of the previous range studied. Fig. 5 shows the projection of the scores for CC1 and CC2 containing 85% of the total variance. However, it must be noted that in this case CC4 (4% of explained variance) was also an interesting CC

420 because it separated superethanol samples from the others, especially from samples I98A and IE10A. In fact, the only ratio involved in this discrimination is the n° 10 containing ethanol (Tab. 5). **It must be noted that superethanol samples altered at 90% still had an intense ethanol peak.** CC4 is then characteristic of the ethanol content of the samples. For consistency with the

425 projections shown in Fig. 3, the CC1 and CC2 axes of Fig. 5 were interchanged. As expected, the clouds of points for each unique sample are wider than in the previous case, but still remain relatively compact, which indicates that altered gasoline samples at 0%, 50% and 90% share a common source and so may still be linked independently of the alteration mode and degree.

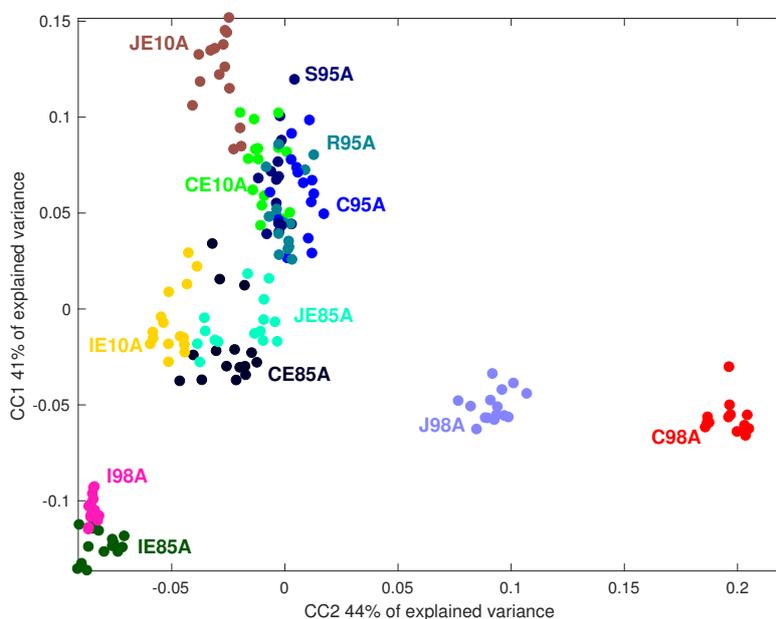


Figure 5: Alteration range between 0% and 90%: scores' projection plot of CC1 versus CC2

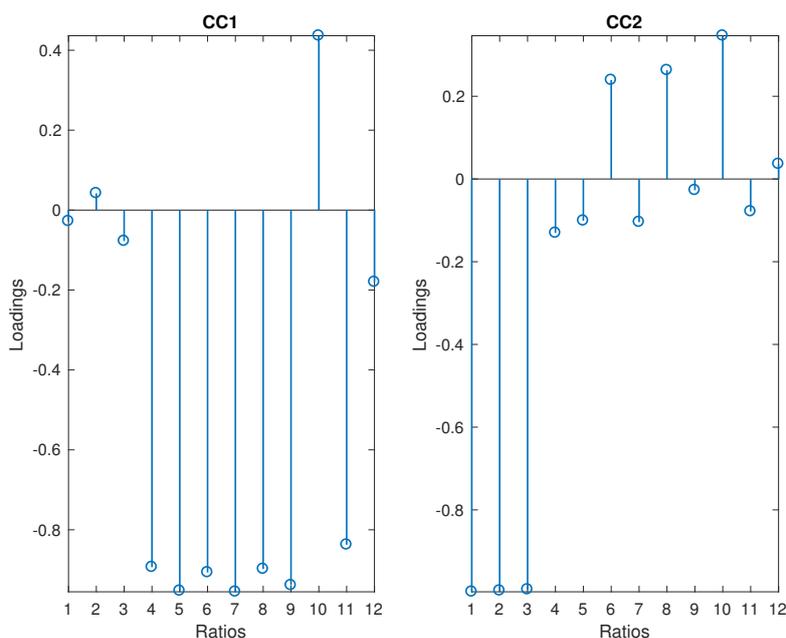


Figure 6: Alteration range between 0% and 90%: loadings of CC1 (left) and CC2 (right)

The selected ratios are not necessarily the same as those selected for the range 0-50%. This point emphasizes the adaptive power of the untargeted chemometrics approach used here since
 430 compounds detected between 0 and 50% may not be detected anymore at 90%. Nevertheless, as previously, the ratios contributing the most (ratios 1, 2 and 3) to the construction of CC2 (Fig. 6, right) all involve 4H-DCPD. The importance of this compound was already discussed above and it is not detailed here again. As for the ratios contributing the most to the construction of CC1 (ratios 4-9 and 11), they involve compounds with high and low octane numbers. The high octane
 435 number compounds are aromatics, as before, and the low octane number compounds are hydrocarbons (isoparaffins and naphthene) with a high number of carbon atoms, e.g. methylnonanes and C9-naphthene. As previously, there is a ratio involving a compound from the column bleed, which is not relevant.

Table 5: Selected ratios for the alteration range between 0% and 90%

Ratio no.	Ion m/z (A)	R_T (A) [s]	Compound A	Ion m/z (B)	R_T (B) [s]	Compound B
1	68	1864	4H-DCPD	111.1	1732	1-methyl-3- <i>n</i> -propylbenzene
2	67	1864	4H-DCPD	113.1	1780	C12-isoparaffin
3	68	1864	4H-DCPD	127.2	1732	1-methyl-3- <i>n</i> -propylbenzene
4	117.1	1585	1,2,4-trimethylbenzene	98.1	1536	2-methylnonane
5	102.1	1220	ethylbenzene	109.1	1247	<i>m</i> -xylene/ <i>p</i> -xylene
6	63	1585	1,2,4-trimethylbenzene	66	1797	1,4-dimethyl-2-ethylbenzene
7	52	1585	1,2,4-trimethylbenzene	112.2	1554	3-methylnonane
8	50	1585	1,2,4-trimethylbenzene	66	1797	1,4-dimethyl-2-ethylbenzene
9	66	1220	ethylbenzene	109.1	1273	C9-naphthene
10	57	1285	3-ethylheptane	47	323	Ethanol
			3-methyloctane			
11	104	1501	1-methyl-3-ethylbenzene	112.2	1554	3-methylnonane
12	79	1308	<i>o</i> -xylene	344.1	2663	Column bleed

The alteration range from 0% to 99% is the most difficult since non-altered gasoline samples
440 are compared with gasoline samples that are almost completely altered. Despite this, it was
interesting to observe that CC1 and CC2 (Fig. 7) explain 91% of the total variance and give
relatively compact clouds of points. This emphasizes the ability of the data treatment workflow
used here to automatically select the most discriminant ratios to assert if two samples share a
common source or not. It must be noted that the CC1 and CC2 axes of Fig. 7 were interchanged
445 as in Fig. 5. Once again, the ratios contributing the most (ratios 1, 2 and 3) to the construction
of CC2 all involve the 4H-DCPD as shown in Fig. 8 (right) and Tab. 6. Concerning CC1, the
loadings show that ratios involving (iso)paraffins and alkylbenzenes contribute the most to its
construction (Fig. 8 left, Tab. 6). **The discussion of these compounds will not be detailed further
for the alteration ranges 0-90% and 0-99% since the discussion proposed for the alteration range
450 0-50% still holds.**

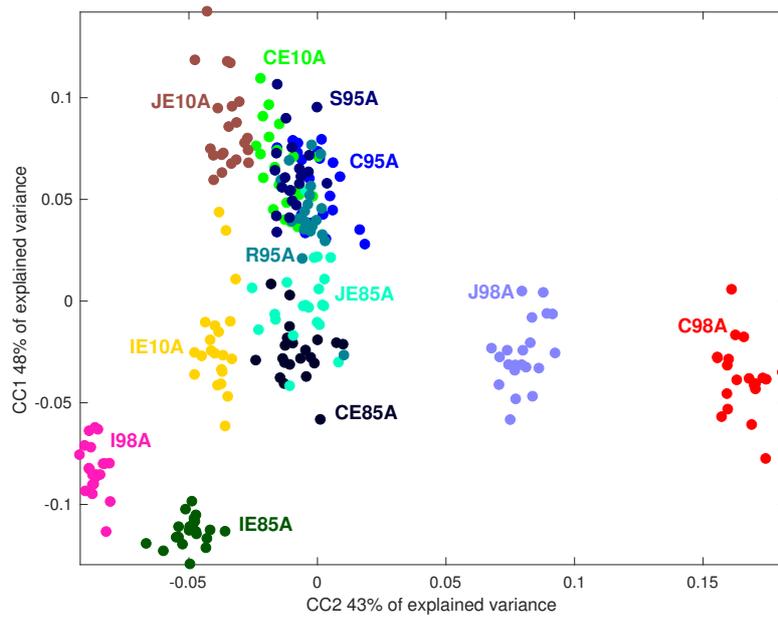


Figure 7: Alteration range between 0% and 99%: scores' projection plot of CC1 versus CC2

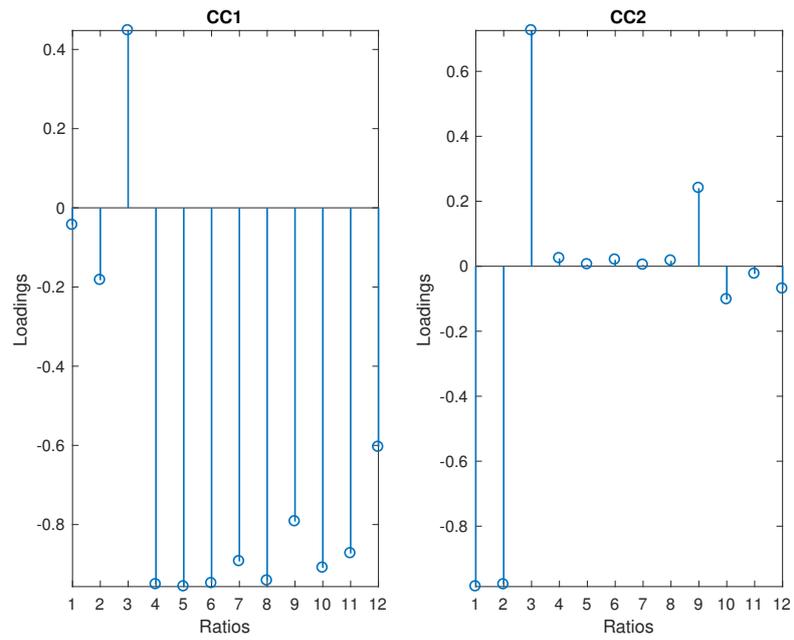


Figure 8: Alteration range between 0% and 99%: loadings of CC1 (left) and CC2 (right)

Table 6: Selected ratios for the alteration range between 0% and 99%

Ratio no.	Ion m/z (A)	R _T (A) [s]	Compound A	Ion m/z (B)	R _T (B) [s]	Compound B
1	67	1864	4H-DCPD	113.1	1780	C12-isoparaffin
2	68	1864	4H-DCPD	113.1	1780	C12-isoparaffin
3	113.1	1780	C12-isoparaffin	122.2	1864	4H-DCPD
4	117.1	1585	1,2,4-trimethylbenzene	112.2	1554	3-methylnonane
5	50	1585	1,2,4-trimethylbenzene	112.2	1554	3-methylnonane
6	52	1585	1,2,4-trimethylbenzene	112.2	1554	3-methylnonane
7	79	1519	1,3,5-trimethylbenzene	112.2	1554	3-methylnonane
8	53	1585	1,2,4-trimethylbenzene	112.2	1554	3-methylnonane
9	77	1657	1,2,3-trimethylbenzene	66	1797	1,4-dimethyl-2-ethylbenzene
10	77	1546	1-methyl-2-ethylbenzene	98.1	1536	2-methylnonane
11	79	1657	1,2,3-trimethylbenzene	84.1	1626	<i>n</i> -decane
12	135.2	1747	1,3-dimethyl-5-ethylbenzene	114.2	1780	C12-isoparaffin

Now that the three ranges of alteration have been covered, the discussion of the CCA results has shown that the compounds involved in the selected ratios were relevant from a chemical point of view. In fact, the compounds were linked to source production characteristics, namely the octane number of the hydrocarbons and the catalytic reforming process, which is used to create high octane blending components from low octane fractions. This evaluation showed that the data treatment approach used in this article may be suitable to provide answers within the framework of the source inference of ignitable liquids. Furthermore, a last point that has not been covered yet concerns the relative retention time of the compounds involved in the calculation of the ratios. Initially, the calculation of the ratios according to Eq. 1 aimed to compensate for the variation created in the analytical response of the samples, which may be caused by the extraction procedure and the alteration effect by evaporation or combustion. The ratios were selected in order to minimize the effect of these interferences during the comparison process and it was observed that the difference between the retention time of the compounds involved in each selected ratios increases with the degree of alteration. For the range 0%-99% (Tab. 6), the mean difference in retention time for the pairs of compounds involved in a ratio was less than a minute, while it was around 1.6 minutes for the alteration range 0%-90% (Tab. 5, without the ratio containing ethanol, which was characteristic of superethanol samples) and 4.5 minutes for 0%-50% (Tab. 4). Hence, the greater the alteration range, the closer the compounds involved in the selected ratios get and the greater the difference in the retention time of the pairs of compounds. This can be explained by the fact that with the increase of the alteration degree, there is also a decrease in the number of points of comparison available since early eluting compounds tend to

disappear. This means that the difference in retention time between the compounds involved in a ratio decreases, increasing their physico-chemical similarities. This also supports the hypothesis that the range of alteration degrees has an influence on the comparison of the gasoline samples and that it would be useful to be able to define narrower ranges of alteration.

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The results of CCA illustrated the possibility to link samples sharing a common source through the projection of the scores, the loadings and associated characterized chemical compounds. A first general observation of the evolution of the projection of the scores was that independently of the alteration degree and mode, by evaporation or combustion, samples sharing a common source are close to each other. In fact, the discrimination of the twelve gasoline samples remains relatively intact with the increase of the alteration range. Returning to Fig. 3, 5 and 7, it can be seen that samples I98A, IE85A, IE10A, J98A, JE10A and C98A have always been discriminated regardless of the alteration range and mode. Remember that in Fig. 5, samples IE85A and IE10A were discriminated along CC4. As for the samples JE85A and CE85A, they have always been close to each other but with some potential of discrimination. However, the remaining samples (CE10A, C95A, R95A and S95A) have always been difficult to differentiate, even for the alteration range between 0% and 50%. This point is very interesting because it means that no discriminating power is created by increasing the alteration range. Samples that were similar for the range 0-50% remain similar at 0-99%. The emphasis is put here on the proximity in space of the gasoline samples sharing a common source. Because twelve gasoline samples are not necessarily representative of a larger population, it is difficult to draw final conclusions about the proximity in space of any samples from different sources. Nevertheless, it is interesting to observe that several situations are present. Some samples are easily discriminated, some are close to each other but with some potential of discrimination, while some could not be differentiated at all. This shows that all kinds of situations that may be encountered if a larger collection of samples is to be used.

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Finally, other chemometric exploratory methods such as Principal Components Analysis (PCA) and Independent Components Analysis (ICA) were also used and the results provided were similar for the three methods. The choice of CCA was based on the philosophy of the methods. Whereas ICA is a blind source separation method, the goal of this study was to evaluate the dispersion of the samples in the multivariate space for a given subsets of variables. The advantage of CCA over PCA is that the ratios responsible for the same dispersion of the samples in the space contribute to the same CC which is not necessarily the case for PCA.

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4. Conclusion

505 The present research confirmed that the alteration of gasoline samples by evaporation or combustion to different degrees drastically modifies their chromatographic profiles. However, it was also shown that by using an appropriate chemometrics approach, it is possible to minimize the effect of the alteration mode (evaporation or combustion) and degree (0% to 99%) when comparing gasoline samples in order to assert if they share a common source or not. Hence, 510 the alteration of the gasoline samples did not compromise the possibility to link samples sharing a common source. The key step in the chemometric workflow used here was the ability of the variable selection method to detect the most discriminant ratios of variables from the data available for comparison. Being able to define a narrower range of alteration when building the models is important to be able to maximize their prediction performances. Moreover, in this 515 work only one support matrix and only 12 unique gasoline samples were considered. Further studies should address the question of the matrix effects when comparing ignitable liquids within a source inference perspective. Plus, given the promising results of the present work **despite the differences between the procedures of alteration by evaporation and combustion**, this approach should be extended to a larger number of gasoline samples. However, it should be noted that the 520 results presented here cannot be generalized to other geographical areas, analytical equipment and procedures. In fact, these results are only valid under the conditions described in this article. To conclude, this exploratory study shows that the possibility to link gasoline samples sharing a common source is not compromised by an alteration by evaporation or combustion over a range from 0% to 99%.

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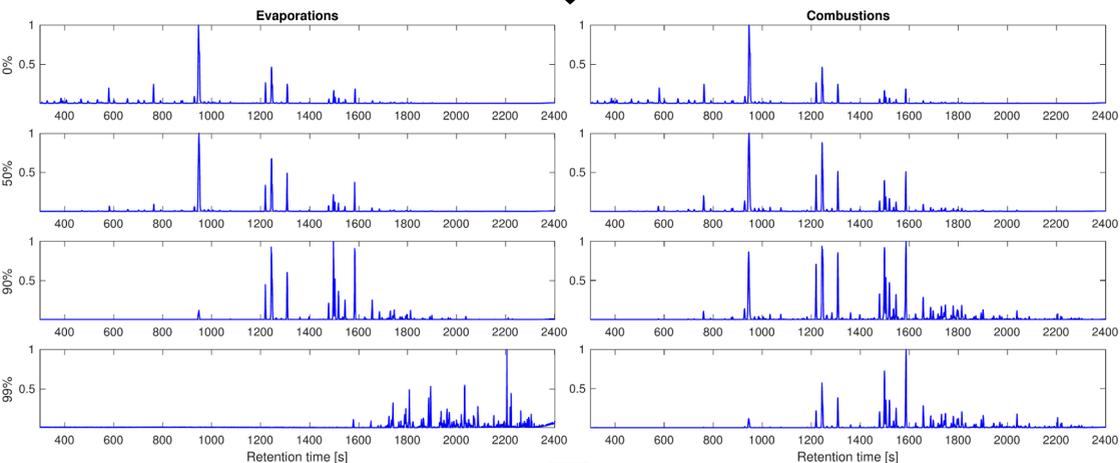
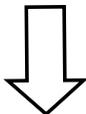
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Gasoline alteration



Feature selection

