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A Computational Procedure in Detecting Adulterated Oleochemical Products

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Vegetable oils can be used as feedstock for the production of a large class of oleochemical products. Unfortunately, price disparities among different kinds of vegetables oils provide an incentive for adulteration by using cheaper substitutes while still claiming otherwise. In this paper, a chemical forensics method for detecting whether or not such an adulteration has been committed is proposed and demonstrated in two case studies, each involving a batch of soap products supposedly produced using 100 % coconut oil and from 75 % coconut oil with 25 % palm oil. The concentration profiles of the fatty acids from soap samples were cross-referenced against known fatty acid concentration fingerprints for coconut oil and for palm oil from the Lipid Handbook through a linear programming model. Executing the model on the sample concentration profiles yielded the back-calculated concentrations of coconut oil and of palm oil used as feedstock with excellent agreement in both cases. The confirmation exhibited in these hypothetical case studies indicates that the procedure can be used in detecting adulteration in other oleochemical products of similar nature, and that the model can be used as a basis in the development of other adulteration detection methods.

1. Introduction

The use of vegetable oils as raw materials for the production of materials has been documented across history, with soap-making practices traceable to the Middle Ages (Dieckelmann and Heinz, 1988) and the first attempts to obtain fatty acids from triglycerides being reported as early as 1883. Today, oleochemicals encompasses a large class of products from soap and rubber to coatings and pharmaceuticals (Zarli, 2020). Unfortunately, the price disparity among different kinds of vegetable oils provides an incentive for the substitution of one type of oil with another cheaper alternative without declaring that such a substitution, or adulteration, has taken place. Several cases of adulteration of similar nature have been documented, one of the most recent being the adulteration of olive oil with rapeseed and corn oil (de Lima et al., 2020). Chemical adulteration has also been detected in other classes of substances, such as honey (Tosun and Keles, 2021), aphrodisiacs (Wang et al., 2018), and coffee (Tavares et al., 2016).

Chemical forensics plays an important role in the detection of such an adulteration. At present, several techniques are available for that purpose, such as swarm-based meta-heuristic algorithms (Xie et al., 2016), principal component analysis (PCA) (Kamal et al., 2019), physico-chemical and spectroscopic techniques (Svečnjak et al., 2019), and chemometrics (Song et al., 2021). While these methods have been established in literature, these have been designed for a specific target audience. However, with the average consumer, who may have access to third-party laboratory services, in mind, no literature describing a simple and easily replicable chemical forensics method has been written. With the expected increase in utilization of oleochemical products (Yeong et al., 2012), such a method will be needed if the adulteration of oleochemical products is to be discouraged. This research gap is addressed in this paper by developing a prototypical linear model, implementable in spreadsheet applications such as Microsoft Excel (Fricke and Schoneberger, 2015), which enables not only the detection of adulteration but also the determination of the degree of adulteration through the calculation of precursor concentrations for comparison with known or expected values, requiring only third-party data which the average consumer has access to. The model formulation is described in the succeeding section, followed by an application on two case studies, and by prospects for future work.

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2. Model formulation

In principle, in the absence of side-reactions and extreme reaction conditions, an oleochemical produced from a precursor with a specific component distribution fingerprint, e.g., fatty acid concentrations, would retain the same fingerprint when tested for its precursor derivatives. If such a product has been made using a mixture of more than two precursors, then the concentration of its precursor derivatives, or components, will be a linear combination of the precursor fingerprints. When these precursor fingerprints are known, back calculating the concentrations of the precursors in the mixture becomes a linear problem of determining the scalar for each precursor derivative. The resulting function defining the concentration of a component i that should be present in sample j is shown in Eq(1):

$$C_{ij} = \frac{\sum_k m_{jk} R_{ik}}{\sum_k m_{jk}};\ \forall i, j \tag{1}$$

where: C_{ij} = actual concentration of component i in sample j;
R_{ik} = reference concentration of component i from a known precursor k;
m_{jk} = scalar of precursor k in sample j;

Preliminarily defining the objective function in Eq(2) as the sum of the square of the differences between the actual and the theoretical concentrations of the components gives:

$$\sum_i {D_{ij}}^2 = \sum_i \left(C_{ij} - \frac{\sum_k m_{jk} R_{ik}}{\sum_k m_{jk}} \right)^2;\ \forall j \tag{2}$$

where: D_{ij} = difference between the sample and the reference concentrations of component i in sample j.

The scalar corresponds to the amount of a precursor k used. Defining P_{jk} in Eq(3) as the concentration of precursor k in sample j, it follows that:

$$P_{jk} = \frac{m_{jk}}{\sum_k m_{jk}};\ \forall j, k \tag{3}$$

and that for all precursors, Eq(4) follows:

$$\sum_k P_{jk} = 1\ \ni\ 0 \leq P_{jk} \leq 1. \tag{4}$$

For an N number of oleochemical products taken from the same batch of production, the concentrations of the precursors for each sample are the same. Hence, for a particular precursor k, the relationships and constraints are given in Eq(5):

$$P_{jk} = P_{j+1,k} = P_k\ ;\ \forall j, k\ \ni\ j \leq N, 0 \leq P_k \leq 1 \tag{5}$$

and the objective function describing the model is arrived at in Eq(6):

$$\sum_i {D_{ij}}^2 = \sum_i \left(C_{ij} - \sum_k P_k R_{ik} \right)^2 \tag{6}$$

where: P_k = concentration of precursor k used in the production of a batch of N oleochemical products.

Minimizing $\sum_i {D_{ij}}^2$ in Eq(6) through variable $P_k, \forall k$ subject to the constraints in Eq(5), yields the concentration of precursor k for a given batch of N oleochemical products.
Only the concentration of the components of each sample C_{ij}, or concentration fingerprints collectively, and at least two suspect precursors, i.e., a null and an alternative, with sufficiently differentiable concentration fingerprints, are required as model inputs. Concentration fingerprints can be acquired through standard laboratory analysis, presenting the advantage of the approach by requiring readily available data. It is presumed, however, that the precursors do not undergo extraneous side-reactions or interactions, as in the saponification of oils in soap production.

3. Case studies

Two hypothetical cases where in each case five samples of soap produced from pure coconut oil were being tested for chemical adulteration with palm oil were used to demonstrate the capabilities of the method, where the shorter fatty acid chains in coconut oil are preferred over the longer fatty acid chains in palm oil due to the lower solubility and lathering ability of soaps made from longer chain oils (Kuntom et al., 1996). In these cases, the model required the concentration fingerprints of each of the samples as input, along with the known concentration fingerprint of coconut oil (Gunstone et al., 1994). Data processing and model optimization with two variables, corresponding to the concentrations of coconut oil and of palm oil, were implemented in Microsoft Excel version 16.47.1 with the Simplex LP Solver Algorithm installed on a machine with a 2.3 GHz Quad-Core Intel Core i7 10th Generation Processor with 16 GB of RAM running a 64-bit macOS version 11.2.3 operating system, with negligible time. The algorithm has been demonstrated to be robust and reliable in handling linear optimization problems (Al-Mhanna et al., 2010).

The free fatty-acid concentration fingerprints for each of the samples for each case are listed in Tables 1 and 2. The concentrations of the components composing the fatty-acid fingerprints are hypothetical but are representative of typical values which a laboratory analysis for a sample of soap produced from 100 % coconut oil (Case A) and 75 % coconut oil adulterated with 25 % palm oil (Case B) would yield:

Table 1: Free Fatty-Acid Concentration Values (in % vol/vol) from Soap Samples for Case A

Sample No.	Caproic Acid C6:0	Caprylic Acid C8:0	Capric Acid C10:0	Lauric Acid C12:0	Myristic Acid C14:0	Palmitic Acid C16:0	Stearic Acid C18:0	Oleic Acid C18:1	Linoleic Acid C18:2
1	0.8	7.6	6.3	47.8	18.3	9.3	2.7	6.4	1.7
2	0.4	7.1	5.9	46.7	18.9	8.8	2.8	6.8	1.8
3	0.7	6.1	6.0	48.0	19.2	8.5	2.7	6.6	1.6
4	0.3	6.9	6.3	47.9	18.6	8.1	2.7	7.2	1.8
5	1.0	6.6	5.3	47.6	18.5	9.1	2.6	6.3	1.5

Table 2: Free Fatty-Acid Concentration Values (in % vol/vol) from Soap Samples for Case B

Sample No.	Caproic Acid C6:0	Caprylic Acid C8:0	Capric Acid C10:0	Lauric Acid C12:0	Myristic Acid C14:0	Palmitic Acid C16:0	Stearic Acid C18:0	Oleic Acid C18:1	Linoleic Acid C18:2
1	0.1	4.2	5.2	37.6	13.9	17.1	3.3	16.8	3.2
2	0.2	3.7	5.0	37.8	14.3	17.5	3.2	17.0	3.5
3	0.1	4.3	4.7	37.6	14.1	16.9	3.0	16.5	3.6
4	0.2	4.0	4.5	37.4	13.8	17.3	3.1	16.6	3.4
5	0.1	4.4	4.6	37.7	13.6	17.0	3.2	17.3	3.7

In Case A, the major components of the samples are lauric acid (C12:0) and myristic acid (C14:0), which is expected from samples containing 100 % Coconut Oil. For Case B, the concentrations of both lauric acid and myristic acid have decreased, while the concentrations of palmitic acid and of oleic acid have increased which is expected with the presence of, or adulteration with, Palm Oil.

The respective average component concentration fingerprints for Cases A and B are shown in Figure 1. The disparity between the fingerprints between the two cases alone is sufficient to establish the adulteration of the samples in Case B with a precursor that is not 100 % coconut oil. Nonetheless, it was the objective not only to detect but also to quantify the degree of adulteration that has taken place.

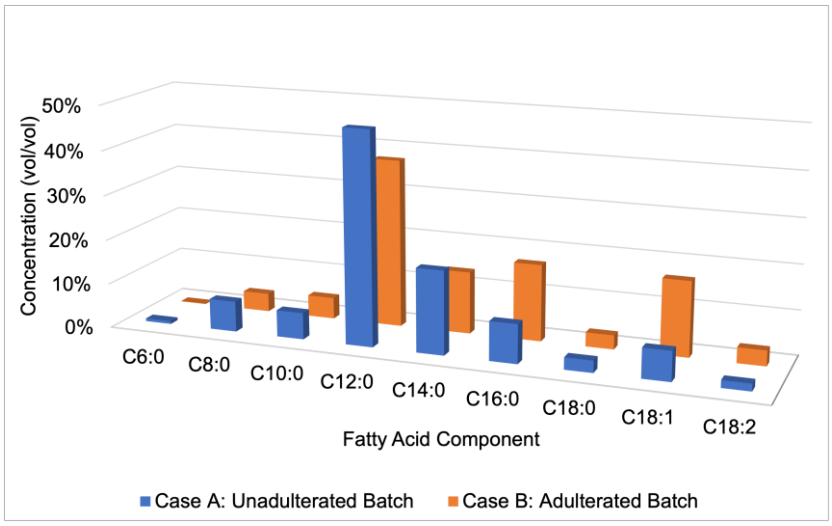

Figure 1: Fatty Acid Concentration Fingerprint for Cases A and B.

Subjecting these data to the linear program, the model output back calculated concentration of coconut oil in Case A was determined to be $P_k = 99.8\ \% \pm 0.2\ \%$. Plotting the model output against the actual concentrations yielded $R^2 = 0.9994$, $m = 0.9983$, shown in Figure 2. The proximity of both R^2 and m to unity and the near-zero value of the y-intercept, b, indicate the soundness of the back calculated concentration of coconut oil. The ideal value of 100 % is within the back calculated interval, indicating the absence of adulteration of this batch of oleochemical products. The similarity between the values of P_k and of m is a matter of coincidence.

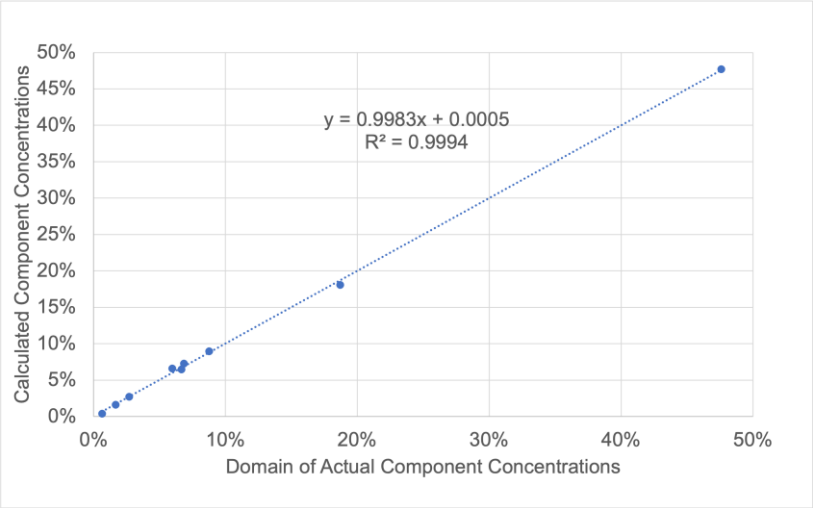

Figure 2: Parity Plot for Case A

Likewise, the model output back calculated concentration of coconut oil in Case B was determined to be $P_k = 75.7\ \% \pm 2.7\ \%$. Plotting the model output against the actual concentrations yielded $R^2 = 0.9940, m = 0.9407$, shown in Figure 3. Similarly, the values of R^2, m, and the y-intercept, b, in the parity plot demonstrate the soundness of the model in back calculating the concentration of coconut oil. In this case, the ideal value of 100 % is not within the back calculated precursor concentration interval, indicating the adulteration of this batch of oleochemical products.

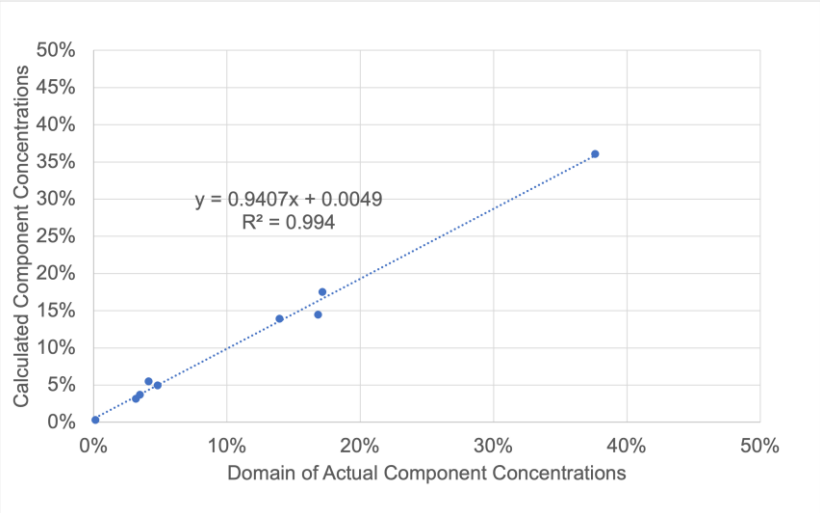

Figure 3: Parity Plot for Case B

A summary between the actual concentration and model output back calculated concentration is shown in Table 3.

Table 3: Summary of Precursor Coconut Oil Precursor Concentrations, Actual vs Model Output

Batch	Actual Concentration	Model Output Concentration
A	100 %	99.8 % ± 0.2 %
B	75 %	75.7 % ± 2.7 %

In both cases, the model correctly determined the amount of coconut oil used, and a combination thereof in case of adulteration, in the production process, yielding 99.8 % for the batch made from 100 % coconut oil, and 75.7 % for the adulterated batch made from 75 % coconut oil. The simplicity and precision of the method demonstrates its extendibility for the detection of adulteration in other classes of oleochemical products whose production processes are of similar nature, and where the detection of adulteration from the analysis of the end-product fingerprints becomes necessary.

4. Conclusions

A computational procedure in detecting adulterated oleochemical products has been developed with the average consumer in mind, requiring only the concentration fingerprints from third-party laboratory analyses and handbook data as model inputs, and a spreadsheet application such as Microsoft Excel. The model minimizes the difference between the component concentration values of a batch of samples and reference concentration values from a known precursor from which the samples should have been produced. Its capability was demonstrated in two case studies, one without adulteration and one with adulteration, correctly identifying the absence (99.8 % ± 0.2 %) or presence (75.7 % ± 2.7 %) of adulteration, supported by decisive regression analysis parameter values. The method can be translated to other classes of oleochemicals of similar nature and can serve as a foundation upon which other models with similar objectives can be built. Studies on the extension of the model to cases where more than two precursors are involved is recommended. The model does not consider the possible non-linear effects of mixing and of the presence of side reactions. Further research on the addition of non-linear terms in the presence of extraneous side reactions is recommended in other classes oleochemicals and case-specific investigations.

Nomenclature

b = parity plot best-fit y-intercept;
C_{ij} = actual concentration of component i in sample j;
D_{ij} = difference between the sample and the reference concentrations for component i in sample j;

i = index for the components in the samples, e.g. Caproic Acid;
j = index for the tested samples from a certain production batch, e.g. Sample No. 1;
k = index for the precursors being investigated, e.g. coconut oil;
m = parity plot best-fit slope;
m_{jk} = scalar of precursor k in sample j;
P_{jk} = concentration of precursor k in sample j;
P_k = concentration of precursor k used in the production of a batch of N oleochemical products;
R^2 = square of Pearson's Coefficient (R); and
R_{ik} = reference concentration of component i from a known precursor k.

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