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# Analytical methods for the detection of adulteration and mislabelling of Raclette Suisse<sup>®</sup> and Fontina PDO cheese

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## Introduction

For food products with registered marks or protected denomination of origin (PDO), protection against adulteration (non-compliance of the technology used for cheesemaking with the Schedule of Conditions) and against mislabelling (incorrect declaration of the geographic origin) are crucial issues for both cheese manufacturers and consumers. The dairy sector is also concerned with this problem. Mislabelling of butter has already been reported and successfully recognised as such by isotope ratio mass spectrometry (IRMS) (1). Milk transportation for cheese making is also a reality, as for instance Dutch milk being transformed in the North of Italy. Analytical control systems should be developed to ensure the genuineness of manufactured dairy products and their correct labelling. Mislabelling of Emmental cheese has already been investigated within a 3-year study (2, 3, and references therein). After the selection of pertinent analytical tools within a preliminary study, it was possible to create and test a mathematical model for the assignment of geographic origin according to a database built on data from more than 180 samples.

A further interesting product in Switzerland is Raclette cheese. As for Emmental, its production area is spread all over Switzerland and is of strong economical importance for the Swiss dairy sector. Importation of Raclette cheese originates largely from France where it is partly produced at lower cost. Mislabelling as Raclette Suisse is therefore conceivable and should be prevented by developing suit-

able analytical tools. Moreover, Raclette Suisse has to be manufactured according to a well-defined procedure. Adulteration within Switzerland is possible by use of e.g., prohibited additives.

In the Aosta Valley in Italy, Fontina PDO cheese is produced in a very traditional way. This cheese type is appreciated in the Italian kitchen. However the production in the restricted PDO area is well below the demand. "Fontal" is produced mostly in the North of Italy and is an industrial imitation making up for the shortage of Fontina. Once again it is important to protect the authentic product with high added value against fraudulent substitution with imitations, either adulteration or mislabelling.

The goal of the current work was to investigate some analytical techniques, based on the knowledge acquired during an Emmental study, for differentiating Raclette Suisse from French Raclette and Fontina PDO from Italian Fontal using primary indicators (not influenced by the milk transformation). Some secondary indicators (depending on the manufacturing technology) were useful to check if a correct milk transformation was applied.

This preliminary study was too small to deliver robust models for origin assignment but was only aimed at pointing to possible ways of doing large scale studies which need to be carried out to ensure good reliability of the models.

## Material and methods

### *Samples*

The twenty-eight Swiss Raclette samples were provided by Raclette Suisse (Berne, Switzerland) from different regions in Switzerland. For the parameters lysozyme, natamycin and sorbic/benzoic acid, only half the Swiss samples were investigated. The fourteen French Raclette cheese samples were purchased directly in four different stores in France. Six were declared to be from Savoie or Haute-Savoie, one from Massif Central and one from Normandy. The origin of the remaining six samples was not known. All Raclette cheese samples were of type "nature".

The sixteen Fontina PDO samples were provided by the "Consorzio produttori Fontina" (Aosta, Italy). They were all produced during the winter in the valley. Ten Fontal cheeses were purchased from four different stores in the North of Italy (Fontal NI). One further Fontal cheese of Swiss manufacture (Fontal CH) was bought in Tessin.

All samples were kept at  $-18^{\circ}\text{C}$  until analysis. Natamycin and sorbic acid were measured in the rind. For the remaining analyses, 2 cm from the rind were discarded. The samples delivered to the various participating laboratories were cut into slices across the whole height of the block. This helped to avoid misinterpretation of results due to gradients in the block.



## Analytical methods

### A) Raclette cheese

The following standard chemical analyses were carried out: water gravimetrically (4), fat according to Gerber van Gulik (5), 12 g/L TCA soluble nitrogen (TCA-SN) and water soluble nitrogen (WSN) according to Kjeldahl (6), sodium chloride potentiometrically with a silver electrode (7) and short chain fatty acids by titration and gas chromatography (8). The pH-value was determined at room temperature using a penetrometric electrode (Mettler-Toledo, article no. 104063123).

Nitrite was determined after fat and protein precipitation. The quantification occurred photometrically at 538 nm after addition of sulfanylic acid amide and N-(1-naphtyl)-ethylendiamine dihydrochloride to the filtrate. Nitrate was determined after reduction to nitrite with cadmium covered with copper (9).

Natamycin was extracted with methanol and quantified using high performance liquid chromatography equipped with a fluorescence detector (HPLC) (10). Sorbic and benzoic acid were derivatised with potassium hexacyanoferrate at pH 8, extracted with methanol and quantified using HPLC and an UV detector (11). Lysozyme was determined in the supernatant of a cheese-sodium chloride-water suspension at pH 4.3 using HPLC and a fluorescence detector (internal ALP method).

For the determination of calcium, approximately 1 g of grated cheese was digested in 5 mL suprapure nitric acid (650 g/kg) at normal pressure. The solutions were analysed with an air-acetylene flame atomic absorption spectrometer (12).

$^{15}\text{N}/^{14}\text{N}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^2\text{H}/^1\text{H}$  and  $^{34}\text{S}/^{32}\text{S}$  ratios were determined in a protein fraction obtained as follows: the grated cheese samples were freeze-dried and then defatted with petroleum ether (Merck AG, Darmstadt, analytical grade) in a soxhlet apparatus. C, N and S were measured by Elementar elemental analyser Vario EL III coupled to an isotope ratio mass spectrometer (IRMS) AP 2003 (Elementar Analysensysteme GmbH, Hanau, Germany, and GVI Instruments Ltd. Manchester, UK). D/H ratios were measured on a Thermo Instruments delta XL plus IRMS coupled with a Thermo Instruments high temperature pyrolysis unit.

The following standards with known ratios were used: a standard casein (Sigma-Aldrich, analytical grade) which had been calibrated in a European research project (SMT4-CT2236-1998) for  $^{13}\text{C}/^{12}\text{C}$  and  $^{15}\text{N}/^{14}\text{N}$ , and later on for  $^2\text{H}/^1\text{H}$  and  $^{34}\text{S}/^{32}\text{S}$  against official reference materials (PEF-1 and NIST-22, V-CDT and silver sulfide, respectively). The values were reported in the  $\delta$ -scale (‰) according to the corresponding international standards (PDB, NBS-22, V-CDT, air  $\text{N}_2$ ). To check the reliability of the analyses, additional IHRM (in house reference materials) of known isotopic composition were used (wheat flour, lactose, sucrose).

### B) Fontina/Fontal cheese

Short chain fatty acids and stable isotope ratios were investigated using the same methods as for Raclette cheese. The activity of the alkaline phosphatase (ALP) was measured photometrically with p-nitrophenylphosphate as substrate (internal

method FAM ME 10202O.211). For the latter, the material for analysis was, in this case only, sampled directly under the rind.

The samples were also investigated using near infrared spectroscopy (NIR). Approx. 150 g grated cheese were placed in a glass Petri dish and measured by diffuse reflection on a Büchi NIRLab N-200 spectrometer (Flawil, Switzerland). The Petri dish rotates around its centre during the measurement. For each sample 64 scans were recorded from 4000  $\text{cm}^{-1}$  to 10000  $\text{cm}^{-1}$  with a spectral resolution of 2  $\text{cm}^{-1}$ .

Lastly the volatile compounds were considered using an MS-based electronic nose of type SMart Nose (LDZ, CH-2074 Marin) equipped with a Combi Pal autosampler (CTC Analytics, CH-4222 Zwingen). The headspace volatiles were preconcentrated using an INDEx syringe (LDZ, CH-2074 Marin). Analytical conditions and data treatment were described elsewhere (13).

### *Statistical analyses*

The NIR spectra were normalised between 0 and 1. Principal component scores from the correlation matrix were computed with PLSPlus/IQ Vs. 5.07 (Thermo Galactic, Salem, NH). In all cases, Principal Component Analysis (PCA) and Discriminant Analysis (DA) were performed using Systat Vs. 9.0 (SPSS Inc., Chicago, IL).

## **Results and discussion**

### *Raclette cheese*

As the regional origin of four French samples was not known, only the categories Swiss and France were considered in a first step. From the 22 parameters measured (Table 1), only the following ten showed significant differences between the countries of origin: chloride, calcium, benzoic acid, lysozyme, natamycin, nitrite,  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and  $\delta^{34}\text{S}$ .

The calcium content was significantly lower in Switzerland. Calcium chloride was most probably added to the milk for processing in France. Sorbic acid, which is allowed as additive for surface treatment, was not found in any sample. The benzoic acid concentration was higher in Raclette Swiss. Benzoic acid in cheese can be produced by three different natural pathways: reversible conversion from hippuric acid in the whole cheese body, breakdown of phenylalanine and autoxidation of benzaldehyde on the surface of smear-ripened cheeses (14). The concentration of this acid depends on several factors such as the composition of the microbial flora, the kind of cheese curing and ripening conditions. The current findings should therefore be confirmed with a higher number of observations. Lysozyme, natamycin and nitrite are additives whose use is authorised by EU and Swiss legislations. However the organisation "Raclette Suisse" voluntarily renounced their use to offer a 100% natural product to consumers<sup>1</sup>. Lysozyme and nitrate/nitrite are often added to

<sup>1</sup>From 2004, colouring additives are also forbidden for the manufacture of Raclette Suisse®. The presence of such additives may be used as further indicator.



Table 1  
Parameters measured in the investigated Swiss and French Raclette cheeses

Parameters	ANOVA	Raclette Suisse (n=28)				French raclette (n=14)			
		<i>x</i>	<i>s<sub>x</sub></i>	Min.	Max.	<i>x</i>	<i>s<sub>x</sub></i>	Min.	Max.
Water (g/kg)	—	418	15	388	447	419	20	388	457
Fat (g/kg)	—	285	14	257	317	286	18	265	338
Chloride (g/kg)	**	22 <sup>A</sup>	3.0	16.6	30	19 <sup>B</sup>	3.8	11.3	24.6
Calcium (g/kg)	***	6.41 <sup>B</sup>	0.56	5.13	7.28	7.00 <sup>A</sup>	0.43	6.42	7.65
pH-value	—	5.65	0.21	5.38	6.19	5.57	0.23	5.16	6.04
TCA-SN (g/kg)	—	6.1	1.1	3.9	7.9	6.2	1.4	3.69	8.36
WSN (g/kg)	—	17.5	6.5	9.8	35.8	15.1	5.2	7.68	26.1
Formic acid (mmol/kg)	—	1.02	0.93	0.22	5.14	0.86	0.33	0.25	1.62
Acetic acid (mmol/kg)	—	12.5	6.3	3.0	25.3	16.0	12	2.96	53.5
Propionic acid (mmol/kg)	—	0.94	3.2	0	16.8	1.0	3.0	0.01	11.4
n-Butyric acid (mmol/kg)	—	0.72	0.57	0.27	2.95	0.51	0.31	0.16	1.22
n-Hexanoic acid (mmol/kg)	—	0.09	0.06	0	0.24	0.08	0.06	0.02	0.25
Benzoic acid (mg/kg)	***	65 <sup>A</sup>	48	7.05	157	15 <sup>B</sup>	13	7.9	60
Sorbic acid (mg/kg)	—	<0.5	—	<0.5	<0.5	<0.5	—	<0.5	<0.5
Lysozyme (mg/kg)	***	<10 <sup>B</sup>	—	<10	10	121 <sup>A</sup>	131	<10	376
Natamycin (mg/kg)	***	<0.05 <sup>B</sup>	—	<0.05	<0.05	7.0 <sup>A</sup>	6.3	<0.05	19.3
Nitrate (mg/kg)	—	1.8	1.0	1	4.3	2.3	1.2	1	4.1
Nitrite (mg/kg)	*	0.18 <sup>B</sup>	0.11	<0.1	0.42	0.33 <sup>A</sup>	0.26	<0.1	1.0
δ <sup>2</sup> H (‰)	***	-123.5 <sup>B</sup>	4.0	-133.1	-116.0	-102.8 <sup>A</sup>	8.0	-115.4	-90.1
δ <sup>13</sup> C (‰)	***	-24.0 <sup>B</sup>	1.0	-25.9	-22.2	-19.6 <sup>A</sup>	2.9	-25.3	-16.3
δ <sup>15</sup> N (‰)	***	5.7 <sup>A</sup>	0.8	4.5	7.4	4.7 <sup>B</sup>	0.7	3.3	5.8
δ <sup>34</sup> S (‰)	***	3.7 <sup>B</sup>	1.9	-1.8	6.2	5.9 <sup>A</sup>	0.9	4.7	7.3

Caption: *x*=mean value; *s<sub>x</sub>*=standard deviation; Min.=minimum; Max.=maximum

ANOVA: ns=not significant, \* *p*≤0.05, \*\* *p*≤0.01, \*\*\* *p*≤0.001

Production sites: A>B (=significantly different contents *p*≤0.01) or AB=A and B overlap by using an univariate discriminant analysis

milk to prevent butyric acid fermentation. The lysozyme concentrations were below the detection limit of 10 mg/kg for all Swiss and for six French samples. The remaining French samples showed concentrations between 56 and 376 mg/kg. The nitrite values were slightly lower in Switzerland but the broad variation ranges within one category rendered this parameter less significant. Natamycin is used as fungicide to protect the smear against moulds. Its concentration was below the detection limit of 0.05 mg/kg in all Swiss samples and in a single French one. The remaining French samples showed values between 0.7 and 19.3 mg/kg. Therefore samples with lysozyme or natamycin value over the detection limit are not genuine for Raclette Suisse, independantly of the origin.

The four isotope ratios,  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{34}\text{S}$ , belong to the group of primary indicators. They were already successfully used for determining the origin of dairy products (1, 15, 16). In cheese making, these are practically only function of the composition of the milk used, and not of the manufacturing technology. The values for the four stable isotope ratios in Raclette Suisse were comparable to those found in Emmentaler Switzerland cheese (17). Even the  $\delta^{13}\text{C}$  values were all typical for maize silage-free zone ( $<-22\text{‰}$ ). In France, two sub-categories could clearly be distinguished with the samples originating from Northwest (NW) and those from East-Central, Savoie and Haute-Savoie (EC). Figure 1 shows the correlation between  $\delta^2\text{H}$  and  $\delta^{34}\text{S}$  in French Raclette and highlights the obvious groups. The parameters with significantly different contents between both French regions are listed in Table 2. The values in the category NW were comparable to those found in the Emmental cheese FT<sub>b</sub> (Bretagne) and the ones in the category EC were in the range of the categories Emmental cheese FR (Savoie) and FT<sub>e</sub> (East-Central) (17). The absolute clear differentiation between both regions brought to light the first cases of fraud. Indeed, two samples labelled with "Fabriqué en Haute-Savoie" were, according to the analytical results, manufactured in a coastal region, or at least the milk used was not from Haute-Savoie. For more details on the interpretation of stable isotope ratios, see in (17).

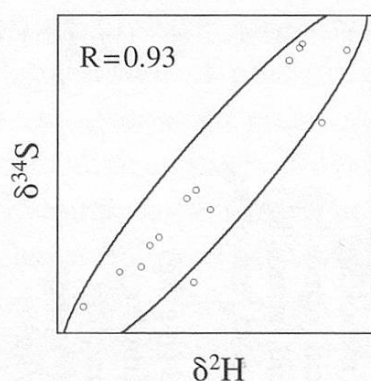


Figure 1 Correlation between the stable isotope ratios  $\delta^2\text{H}$  and  $\delta^{34}\text{S}$  in French Raclette cheese. The five samples with the highest  $\delta^2\text{H}$  ratio were from the northwest region of France

Table 2  
Parameters with significant differences between France Northwest and France Centre/East

Parameters	<i>Raclette Suisse (n=28)</i>		<i>Raclette Centre/East (n=9)</i>		<i>Raclette Northwest (n=5)</i>	
	<i>x</i>	<i>s<sub>x</sub></i>	<i>x</i>	<i>s<sub>x</sub></i>		
Acetic acid (mmol/kg)	12.5 <sup>B</sup>	6.3	21 <sup>A</sup>	13	5.6 <sup>B</sup>	1.9
Calcium (g/kg)	6.41 <sup>B</sup>	0.56	7.20 <sup>A</sup>	0.40	6.64 <sup>AB</sup>	0.20
δ <sup>2</sup> H (‰)	-123.5 <sup>C</sup>	4.0	-108.0 <sup>B</sup>	4.0	-93.4 <sup>A</sup>	2.2
δ <sup>13</sup> C (‰)	-24.0 <sup>C</sup>	1.0	-21.2 <sup>B</sup>	2.2	-16.72 <sup>A</sup>	0.33
δ <sup>15</sup> N (‰)	5.7 <sup>A</sup>	0.8	4.41 <sup>B</sup>	0.39	5.12 <sup>AB</sup>	1.04
δ <sup>34</sup> S (‰)	3.7 <sup>C</sup>	1.9	5.29 <sup>AB</sup>	0.39	7.05 <sup>A</sup>	0.32

Caption: *x*=mean value; *s<sub>x</sub>*=standard deviation

Production sites: A>B>C (=significantly different contents  $p \leq 0.01$ ) or AB=A and B overlap by using an univariate discriminant analysis



A PCA using the factors  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and  $\delta^{34}\text{S}$  was carried out. The scores of the first two principal component explained 74% of the total variability and allowed a good separation of the regions of origin (Figure 2).

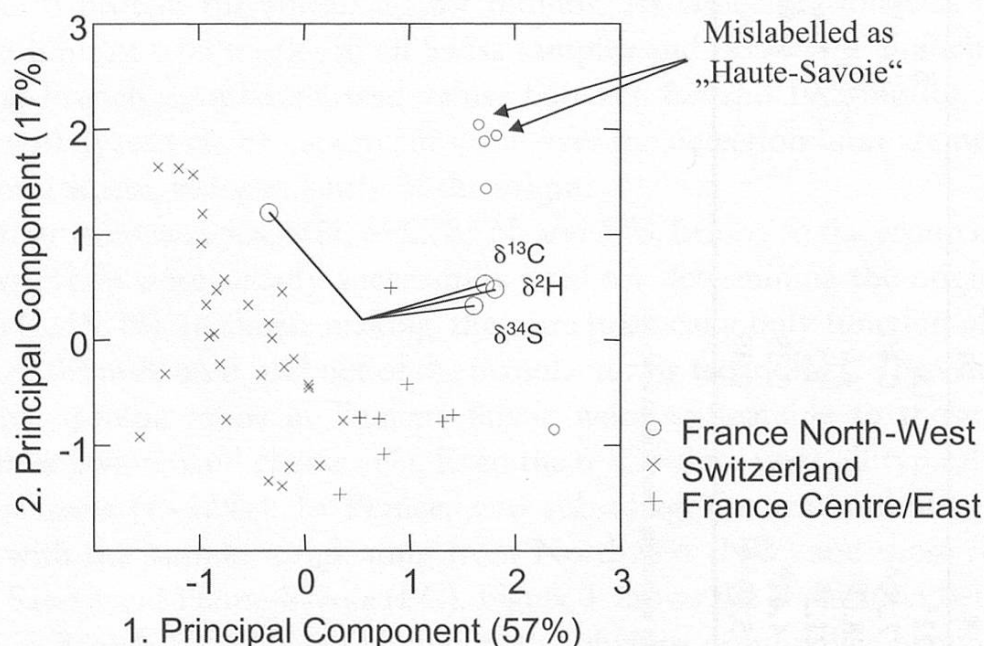


Figure 2 Scores of principal component analysis using the factors  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and  $\delta^{34}\text{S}$ . Discrimination between Raclette cheese originating from Switzerland, France North-West and France East/Centre. Evidence of mislabelling of two samples

### Fontina and Fontal cheese

The results of the various parameters measured are listed in Table 3. To be recognised as PDO, Fontina cheese must be made from raw milk. Usually, the milk used for the manufacture of industrial semi-hard cheese is pasteurised. Indeed the results of the ALP activity indicated clearly that pasteurisation was carried out in the investigated samples originating outside the Aosta Valley. For Fontina PDO, the ALP values varied between 1799 and 5046 IU/kg. Only one Fontal cheese had with 56 IU/kg an ALP activity over the detection limit. ALP is therefore a perfect indicator for recognising imitations of Fontina made using pasteurised milk. The volatile short-chain acids did not deliver useful results.

The parameters  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  also showed significant difference. The higher  $\delta^2\text{H}$  values encountered in Fontal NI may be explained by the proximity to the sea compared to the Aosta Valley and the region where Fontal CH was manufactured. The reason for the higher  $\delta^{13}\text{C}$  value in Fontal NI is clearly the use of maize silage. The significantly lower  $\delta^{15}\text{N}$  values in Fontina PDO can be explained by the very extensive agriculture encountered in this alpine valley. Figure 3 shows

Table 3  
Parameters measured in the Fontina and Fontal cheeses investigated

Parameters	ANOVA	Fontina PDO (n = 16)		Fontal NI (n = 10)		Fontal CH (n = 1)	
		$\bar{x}$	$s_x$	$\bar{x}$	$s_x$	$\bar{x}$	$s_x$
ALP1 (IU/kg)	***	2752 <sup>A</sup>	1011	6 <sup>B</sup>	18	0 <sup>B</sup>	—
$\delta^2\text{H}$ (‰)	***	-127.66 <sup>B</sup>	5.3	-110.7 <sup>A</sup>	5.1	-123.8 <sup>AB</sup>	—
$\delta^{13}\text{C}$ (‰)	***	-23.49 <sup>B</sup>	0.90	-19.80 <sup>A</sup>	2.2	-24.68 <sup>B</sup>	—
$\delta^{15}\text{N}$ (‰)	***	4.51 <sup>B</sup>	0.49	5.72 <sup>A</sup>	0.77	6.29 <sup>A</sup>	—
$\delta^{34}\text{S}$ (‰)	—	4.52	1.20	5.26	0.75	3.76	—
Formic acid (mmol/kg)	—	1.43	0.34	1.8	0.85	2.12	—
Acetic acid (mmol/kg)	—	10.57	3.95	10.6	5.02	16.3	—
Propionic acid (mmol/kg)	—	0.41	0.66	0.2	0.35	0.08	—
n- Butyric acid (mmol/kg)	—	0.48	0.47	1.1	0.78	0.78	—
n-Hexanoic acid (mmol/kg)	—	0.08	0.03	0.2	0.25	0.19	—

Caption:  $\bar{x}$ =mean value;  $s_x$ =standard deviation; ANOVA: ns=not significant, (\*\*\*)  $p \leq 0.001$

Production sites: A>B (=significantly different contents  $p \leq 0.01$ ) or AB=A and B overlap by using an univariate discriminant analysis

<sup>1</sup> Alkaline phosphatase

PDO=Protected denomination of origin

NI=North Italy

CH=Switzerland

the scores of a principal component analysis using the parameters  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ . The separation between the regions of origin was perfect. The ratio  $\delta^{34}\text{S}$  did not deliver useful information.

An interesting discrimination could also be achieved using the electronic nose. A PCA combining the signal of the mass-to-charge ratios 45, 83 and 86 showed a good separation between the two groups Fontina PDO and Fontal NI/CH (Figure 4). As volatile compounds are very sensitive to variations in manufacture, further investigations should be carried out to understand the origin of these differences, before using this technology for origin assignment.

Finally, principal component scores were extracted by PCA from the NIR data set and a discriminant analysis was applied on the first 10 scores. In the Jackknifed classification, only 50 % correct assignment was achieved, which is not sufficient.

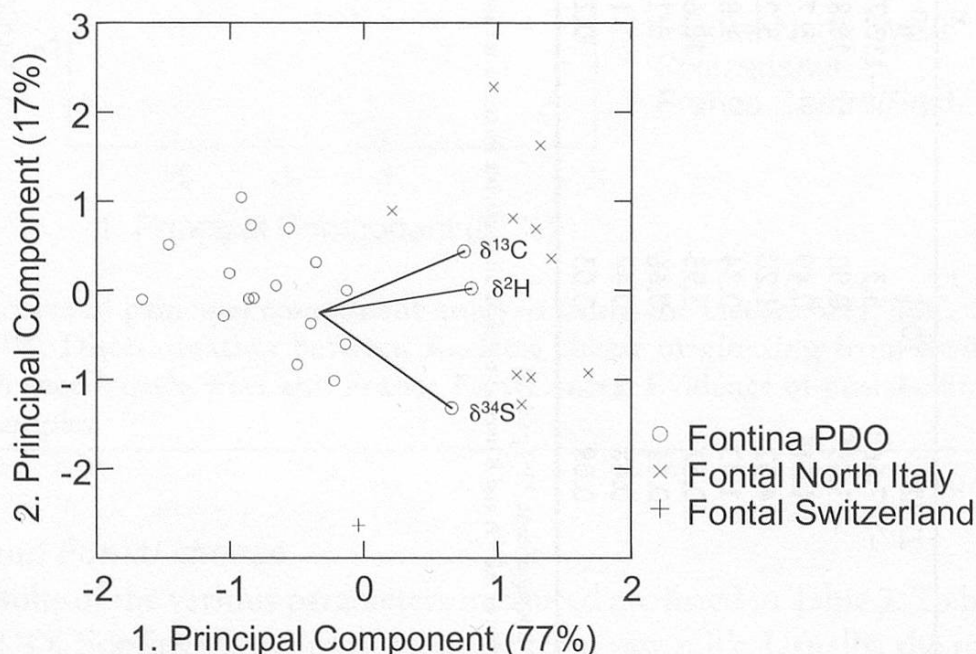


Figure 3 Scores of principal component analysis using the factors  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ . Discrimination between the true Fontina PDO, Fontal cheese produced in the North of Italy (NI) and in Switzerland (CH)



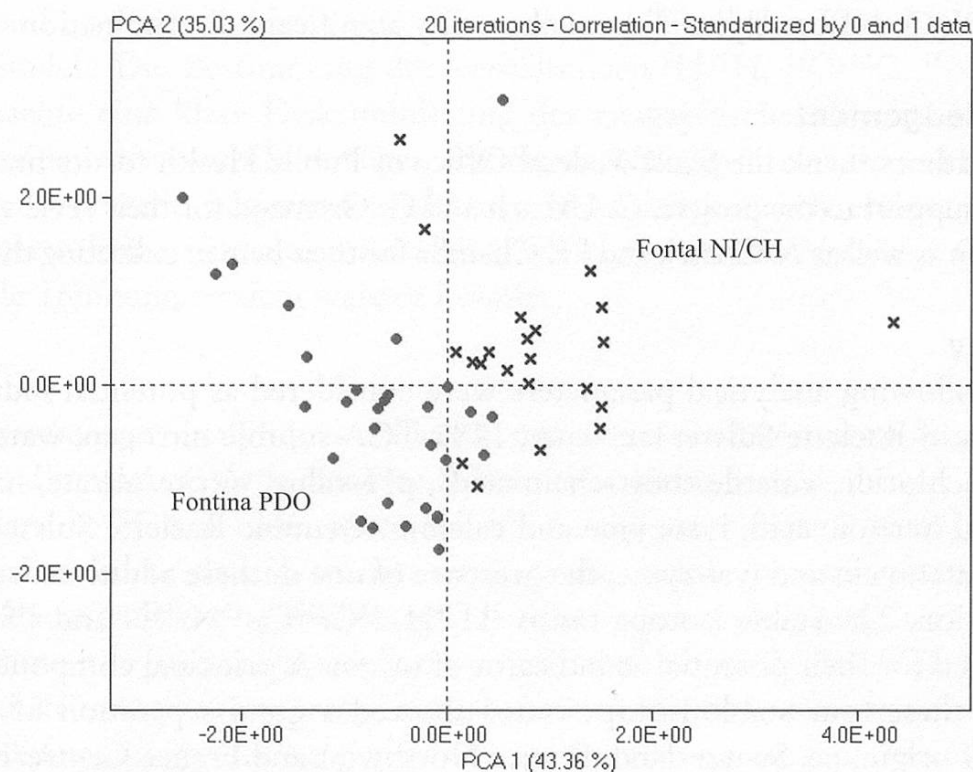


Figure 4 Scores of principal component analysis using the factors  $m/z=45, 83, 86$  from the electronic nose. Discrimination between the true Fontina PDO and Fontal cheese produced in the North of Italy (NI) and Switzerland (CH)

## Conclusion

Apart from Emmentaler Switzerland, Raclette Suisse is a cheese typically made in Switzerland which could be exposed to fraudulent substitution with foreign imitations. Primary indicators such as stable isotope ratios are very useful in food traceability. By measuring the stable isotope ratios  $\delta^2\text{H}$  and  $\delta^{34}\text{S}$ , two subcategories were clearly formed within the French samples, i.e. northwest and centre/east France. A principal component analysis (PCA) using the four stable isotope ratios  $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$  and  $^{34}\text{S}/^{32}\text{S}$  resulted in a good separation in the three categories. These analyses brought to light two likely cases of mislabelling. Furthermore, the presence of lysozyme or natamycin, both additives allowed by EU and Swiss legislations but not by the organisation "Raclette Suisse", can be used to detect imitations, independently of the origin.

Fontina PDO is a cheese produced exclusively in the Aosta Valley. Imitations are manufactured in the North of Italy and in Switzerland and sold under the name Fontal. It was possible to discriminate between the true Fontina PDO and all investigated imitations thanks to the alkaline phosphatase (ALP) activity. The former is a raw milk cheese with enzyme activity higher than 1700 IU/kg whereas the investigated Fontal were made from pasteurised milk with ALP activity lower than 56 IU/kg, mostly of 0 IU/kg. A PCA using the parameters  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$

allowed a perfect separation between Fontal north Italy, Fontal Switzerland and Fontina PDO. NIR analyses did not show any significant discrimination.

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## Summary

The following analytical parameters were considered as potential indicators of imitations of Raclette Suisse: fat, water, 12 %-TCA soluble nitrogen, water soluble nitrogen, chloride, volatile short-chain acids, pH-value, nitrite/nitrate, natamycin, sorbic and benzoic acid, lysozyme and calcium. Genuine Raclette Suisse does not contain natamycin and lysozyme; the presence of one of these additives was a proof for imitation. The stable isotope ratios  $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$  and  $^{34}\text{S}/^{32}\text{S}$  were investigated for their potential as indicator of origin. A principal component analysis using these four stable isotope ratios showed a good separation of the three regions of origin, i.e. Switzerland, France Northwest and France Centre/East. Mislabelling of origin might be detected on this way.

For determining the genuineness of Fontina PDO, the alkaline phosphatase and the volatile short-chain acids were measured. The genuine Fontina cheese was clearly differentiated from imitations (Fontal cheese) by the alkaline phosphatase activity due to different heat treatments of the milk. The measurement of the isotope ratios  $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$  and  $^{15}\text{N}/^{14}\text{N}$  allowed a perfect separation of the samples according to their origin. Further measurements were carried out using a NIR spectrometer and a MS-based electronic nose. The former equipment did not deliver useful results whereas a fair separation was achieved using the latter equipment.

## Zusammenfassung

Die folgenden analytischen Parameter wurden als potenzielle Indikatoren für Nachahmungen von Raclette Suisse betrachtet: Fett, Wasser, 12 %-TCA löslicher Stickstoff, wasserlöslicher Stickstoff, Chlorid, flüchtige kurzkettige Säuren, pH-Wert, Nitrit/Nitrat, Natamycin, Sorbin- und Benzoesäure, Lysozym und Kalzium. Echte Raclette Suisse Käse enthalten kein Natamycin und Lysozym; die Anwesenheit einer dieser Zusatzstoffe ist ein Hinweis für Nachahmungen. Die Verhältnisse der stabilen Isotope  $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$  und  $^{34}\text{S}/^{32}\text{S}$  wurden für deren Potenzial als Herkunftsindikator untersucht. Eine Hauptkomponentenanalyse mit diesen vier Isotopenverhältnissen zeigte eine Trennung der Herkunftsregionen, d.h. Schweiz, Frankreich Nordwesten und Frankreich Zentrum/Osten. Falsche Herkunftsdeklarationen könnte auf diese Weise detektiert werden.

Für die Bestimmung der Authentizität von Fontina GUB wurden die alkalische Phosphatase und die flüchtigen kurzkettigen Säuren herbeigezogen. Echte



Fontina GUB unterschieden sich klar von Nachahmungen (Fontalkäse) dank der alkalischen Phosphatase-Aktivität auf Grund unterschiedlicher Hitzebehandlungen der Kessmilch. Die Bestimmung der Verhältnissen  $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$  und  $^{34}\text{S}/^{32}\text{S}$  machte eine klare Diskriminierung der geographischen Herkunft möglich. Ausserdem wurden noch Messungen mit einem NIR-Spektrometer und einer auf Massenspektrometrie basierenden elektronischen Nase durchgeführt. Das erste Gerät lieferte keine eindeutige Resultate, während mit dem zweiten Gerät eine akzeptable Trennung erreicht werden konnte.

## Résumé

Les paramètres analytiques suivants ont été considérés comme marqueurs potentiels d'imitations de la Raclette Suisse: teneurs en matière grasse, eau, azote soluble dans le TCA à 12 %, azote soluble dans l'eau, chlorure, acides volatils à courte chaîne, valeur de pH, nitrite/nitrate, natamycine, lysozyme et calcium. La véritable Raclette Suisse ne contient pas de natamycine et de lysozyme; la présence de l'un deux est la preuve d'une imitation. Les rapports  $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$  et  $^{34}\text{S}/^{32}\text{S}$  ont été mesurés pour leur potentiel comme indicateur d'origine. Une analyse discriminante par composantes principales incluant ces quatre rapports isotopiques montre une séparation des échantillons de fromage à raclette selon leurs trois régions d'origine, à savoir la Suisse, le Nord-Ouest et le Centre/Est de la France. Des fausses déclarations d'origine pourraient être détectées de cette manière.

En vue de l'authentification de la Fontina AOC, les teneurs en phosphatase alcaline et en acides volatils à courte chaîne ont été examinés. La véritable Fontina AOC se différenciait clairement des imitations (fromage de type Fontal) par l'activité de la phosphatase alcaline après les différents traitements thermiques appliqués au lait. La mesure des rapports  $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$  et  $^{34}\text{S}/^{32}\text{S}$  a permis une parfaite séparation des échantillons en fonction de leur origine. Des mesures ont également été effectuées à l'aide d'un spectromètre NIR et d'un nez électronique basé sur la spectrométrie de masse. Le premier cité n'a donné aucun résultat significatif alors que le second a permis une séparation acceptable.

## Key words

Authenticity, Raclette, Fontina, Fontal, PDO, Cheese, Lysozyme, Natamycin, Stable isotope ratio, Calcium, Alkaline phosphatase

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