Universität Rostock Traditio et Innovatio
HelmholtzZentrum münchen
Deutsches Forschungszentrum für Gesundheit und Umwelt
JOINT MASS SPECTROMETRY CENTRE

ON-LINE PUFF RESOLVED ANALYSIS OF CIGARETTE SMOKE FOR PRODUCT PROFILING USING SOFT-PHOTOIONISATION MASS SPECTROMETRY

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Introduction & Method

The cigarette market continues to enjoy high demand from consumers. In doing so, the cigarette industry in Germany generated a turnover of 21.6 billion euros in 2018 [1]. Such high profits also attract the interest of the black market. According to an estimate, 30% of all cigarette sales around the world are counterfeited [2].

The worrying aspect of such a large number of counterfeits and the very limited possibilities of identifying them is that there is no control of the composition of tobacco and other harmful additives for such cigarettes. The now strictly regulated limits of nicotine, tar and carbon monoxide content as well as already issued prohibitions of additives, which are highly carcinogenic, do not apply to fake cigarettes.

The cigarette brands on the German market and in large parts of the world come from only a few manufacturers. For example, the four largest tobacco companies in Germany had a market share of approx. 87% in 2017.

This study is focusing on creating clearly identifiable profiles of different cigarette brands. The differences between smoke constituents and their ratio are investigated. Based on this, the aim of this approach is to present a way in which counterfeit or defective cigarettes can be distinguished from the original ones by chemical analysis .

Figure 1: Experimental setup with the commercial available LM2X Smoke Analyzer from Borgwaldt KC and Photonion GmbH (Germany)

The test setup consists of a two-channel smoke machine from Borgwaldt KC, a deuterium lamp as ionization source for photoionization by means of SPI (Single Photon Ionization) and a reflectron-oaTOF mass spectrometer (orthogonal acceleration time of flight). The ISO standard smoke protocol was used with the following parameters: puff volume: 35 ml bell shape; puff duration 2 seconds; puff to puff delay: 60 seconds.

Hersteller	Marke	Nikotin / mg	Teer / mg	CO / mg
Phillip Morris International	Marlboro Red	0,8	10	10
	Marlboro Gold	0,5	6	7
Reemtsma*	Gauloises Red	0,6	7	9
	Gauloises Blue	0,8	10	10
British American Tobacco	Pall Mall Red	0,8	10	10
	Pall Mall Blue	0,6	7	8
	Pall Mall ohne Filter	0,8	10	7
	Lucky Strike Red	0,8	10	10
Japan Tobacco International	Camel Filters	0,8	10	10
	Winston Black	0,8	10	10

Table 1: Examined cigarette brands with associated manufacturer and their nicotine, tar and carbon monoxide content per cigarette [3]. * Reemtsma is a subsidiary of the tobacco company Imperial Tobacco Group.

PCA – Principle Component Analysis

Mass spectra contain a great deal of information, which is available in the form of thousands of data points. This wealth of information can be explored using principal component analysis (PCA).

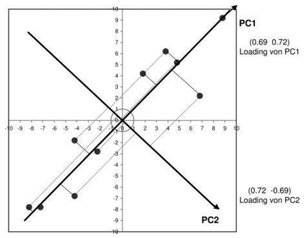

Figure 2: Graphical representation of a principal component analysis with original coordinate system *[Kessler, Waltraud: Multivariate Datenanalyse für die Pharma-, Bio- und Prozessanalytik. Wiley-VCH, 2006]*

Applications, Results & Discussion

The PCA enable a fast overview and comparison option for multivariate data. To ensure good comparability between the cigarette brands examined, the raw data is reduced by three times the blank before TIC standardization. If a negative signal occurs, it is set to zero. Generally the first component explains the includes the main observed variation. By having a look into the loadings, the main influencing signals are nicotine (162 m/z) and isoprene (68 m/z). According to the first principal component, only the non-filter and research cigarettes, as well as the Pall Mall Blue and Marlboro Gold brands can be identified as distinct groups. To archive a further grouping or separation, the subordinate principal components need to be taken into account. In the figures they are shown up to the fourth principal component together with the appearing clusters. In a second step of the study, the influence of defects in the cigarettes should be investigated. On the one hand to show the capabilities for quality control purposes, but also to have a hint for counterfeit cigarettes, typically not having the same structure and tobacco as the original. The results can be seen in figure 4.

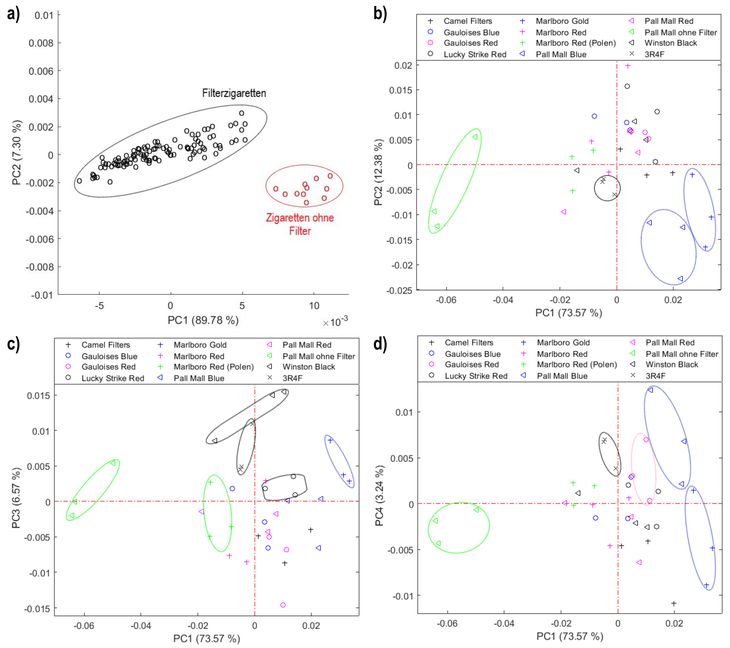

Figure 3 a): PCA scores of cigarettes with filter (black) and without filter (red) **b-d)** PCA scores and groupings of different filter cigarette brands and types by main component 1 vs. main components 2 to 4

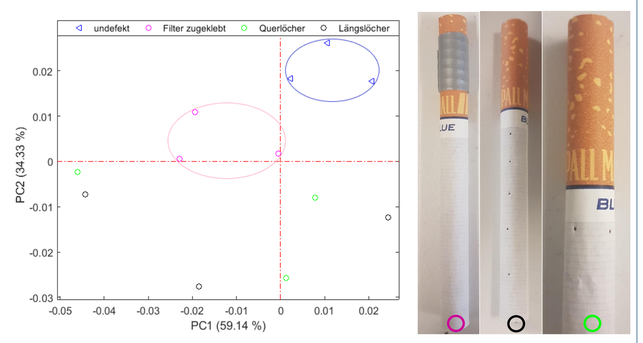

Figure 4: Investigated cigarettes with (magenta) taped filter with adhesive tape (black) holes in the cigarette paper, along the cigarette (green) holes in the cigarette paper, in front of the filter the filter.

Conclusion

Even it is not easy to identify significant difference between the cigarette brands, defects in the structure of the original cigarettes can be detected very well by the principal component analysis. Thus, this method could also be a way to identify counterfeit cigarettes.

Acknowledgements

photonion

Photonion GmbH is an innovative company providing customized solutions for monitoring of chemicals using mass spectrometry with soft ionization methods such as photo ionization.

PHOTO-TOF-MS
SMOKE-PHOTO-TOF-MS
PHOTO-ATOF-MS
TG-PIMS

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