PT 8 - Loureau - Hoffmann analytes: Influence of cigarette paper and filter ventilation

Authors: BIESSE J.P.; CLARISSE G.; VIDAL B.; DUMERY B.; LE MOIGNE C.; LE BEC L.; LE-BOURVELLEC G.; LOUREAU J.M

Hoffmann analytes: Influence of cigarette paper and filter ventilation.

Jean-Paul BIESSE*, Grégory CLARISSE*, Bernard VIDAL*, Bernard DUMERY*, Christophe LE MOIGNE**, Lanig LE BEC**, Gilles LE-BOURVELLEC** , Jean-Marie LOUREAU**
** : Altadis, Les Aubrais, France*
*** : Papeteries de Mauduit, Quimperlé, France*

Summary

Having a tool that can predict the Hoffmann analytes has become necessary, not only because of regulations, but also as a reference for the chemical composition of smoke for the PREPS.

The work presented in this paper is a systematic study on the role of cigarette paper main parameters, (porosity and citrate), and on filter ventilation on all of the Hoffmann analytes.

To conduct this systematic study, we have used a face centred central composite design. This type of matrix allows a global analysis on the parameters studied, taking into account possible relationship of the second order, and possible interactions between the parameters studied.

For the 3 levels of variations requested in these type of study we have used:

- Cigarette paper porosity: 20 ; 50 ; 80 Coresta
- Amount of Na/K citrate: 0.6 ; 1.3 ; 2.0 %
- Levels of filter ventilation: 0 ; 20 ; 40 %

The blend used in this study is a standard American blend.

Cigarettes were smoked for all Hoffmann analytes, including tar, nicotine and carbon monoxide.

Data analysis from this study lead to a number of conclusions, which are presented:

- Like for Tar and CO, filter ventilation is a major tool to reduce most of the Hoffmann analytes; the porosity of cigarette paper, to a lesser extent, also plays a significant role.
- The classification of the analytes in group of production was difficult, as, depending on the design tool used, the different analytes do not follow the same trends.
- Reliable trends for a majority of the analytes are given, allowing predictions from the change in filter ventilation and cigarette paper design.

The results for formaldehyde are also detailed.

Introduction

As already described at the Coresta 2003[1](1), we have conducted a matrix study on the influence of filter ventilation, cigarette paper porosity, and on the amount of citrate in the cigarette paper on the Hoffmann analytes.

The matrix was a face centred composite design that allows seeing linear relationships, possible interactions between the parameters studied, and squared terms for the main factors.

The levels used for the parameters studied were:

	Porosity	**Citrate Na/K**	**Filter Ventilation**
Level 1	20	0,6	0
Level 0	50	1,3	20
Level 1	80	2,0	40

Materials and Methods

The cigarettes were king size, using a standard American blend.

All the analytes were measured at Ökolab including tar, nicotine and CO, using the methods below.

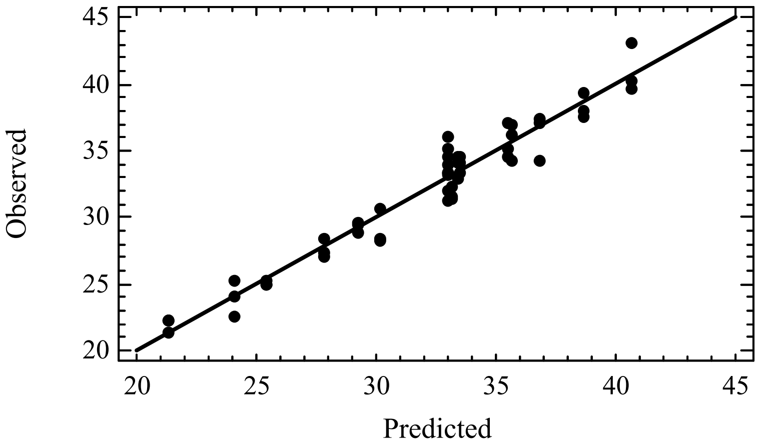
- **Hoffmann analytes**
  - TSNA (NNN, NAT, NAB and NNK) : GC - TEA
  - Phenols : HPLC – fluorescence
  - Heterocycles, unsaturated components, aromatic hydrocarbons, aromatic amines and PAH : GC - MS
  - Ammonia : cation exchange chromatography
  - Hydrogen Cyanide : ion selective electrode
  - Carbonyls : DNPH derivatives - HPLC
  - Metals : AAS, ICP
  - Nitric oxide : puff by puff analysis - NO analyser

Results and Discussions

- Model reliability:

To check for the reliability of our model, we first checked and confirmed that what we obtained for tar, nicotine and CO were corresponding to what was already known[1].

We then checked for the reliability of the models found for each analyte. We did it by plotting observed against predicted values: example for benzene.



Model obtained for benzene

Benzene (µg/cig.) = $44.78 - 1.56\ 10^{-1} \times \text{Perm} - 2.45 \times \text{Cit} - 1.05\ 10^{-1} \times \text{FV} + 4.90\ 10^{-2} \times \text{Perm} \times \text{Cit} - 4.53\ 10^{-3} \times \text{FV}^2$

R^2=93.7%

We have classified the R squared in three categories: above 90%, from 90 to 80%, and below 80%:

R^2 adjusted > 90 %		80 < R^2 adjusted < 90 %		R^2 adjust
Analyte	**R^2 adjusted %**	**Analyte**	**R^2 adjusted %**	**Analyte**
CO	98.2	Pyridine	88.9	Isopre
TAR	96.7	Cadmium	88.9	N
EMK	94.5	Propionaldehyde	88.9	Fluoranthre
NO	94.4	Acetone	88.8	Benzo[ghi]peryle
Benzene	93.7	Total TSNA	87.6	Phenanthre
Nicotine	93	Toluene	87.2	Quinoli
Crotonaldehyde	92.8	Benzo[b]fluoranthene	86.8	N
Total carbonyls	92.3	Total PAH	86.6	Merc
Acrylonitrile	91.8	Resorcinol	86.5	Pyre
Butyraldehyde	91.5	NNN	86.1	Chryse
Acetaldehyde	91.3	Acrolein	85.6	1.3-Butadie
Formaldehyde	91.1	HCN	85.5	Anthrace
		Indeno(123-cd)pyrene	85.4	Le
		Benzo[a]pyrene	85.2	Catec
		NAT	83.4	N
		Benzo[e]pyrene	81.4	Hydroquino
		Total metals	81.3	Phe
		Styrene	81.0	Arse
		Benz[a]anthracene	80.7	m-.p- Cre

Benzo[k]fluoanthene	80.2	o-Cre
		Nic
		4-Aminobiphe
		3-Aminobiphe
		2-Aminonaphtale
		1-Aminonaphtale
		Dibenz(ah)anthrace
		Chromiu
		Seleniu

For most of the analytes, the matrix can be used to make reliable predictions:

. Tar, Nicotine, CO,
. NO
. PAH
. TSNA
. Carbonyls
. Volatiles and semi volatiles

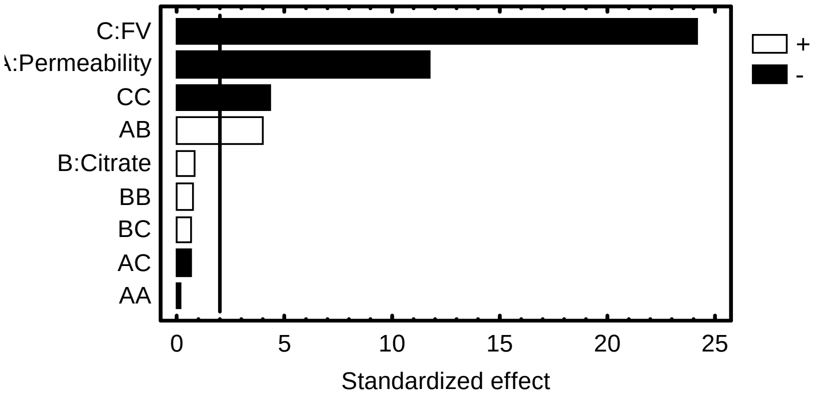
Because of low R^2, and high variations on the results, the model cannot be used for:

- Metals
- Aromatic amines, Amonia
- HCN
- Phenolic compounds

Prediction models:

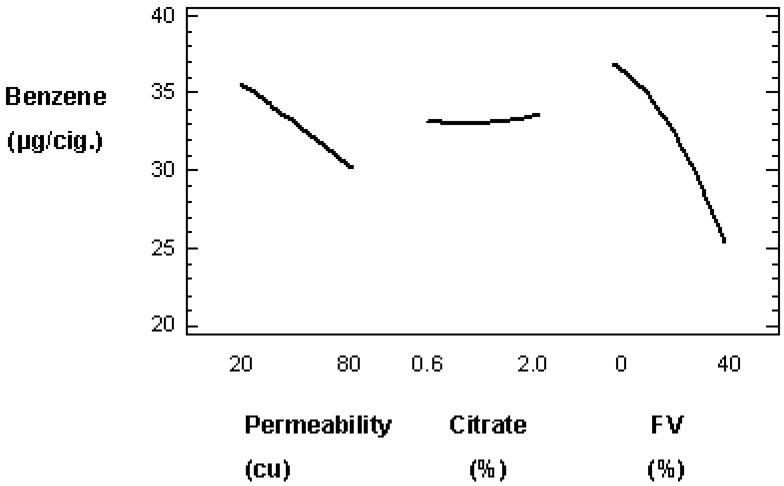
What we have tried to do was to classify the analytes in groups of prediction. To do so, we had not only to look at the global influence of each parameter on the analyte, but also at the type of relationship (linear or quadratic), and the possible interactions between the parameters.

Example: benzene:



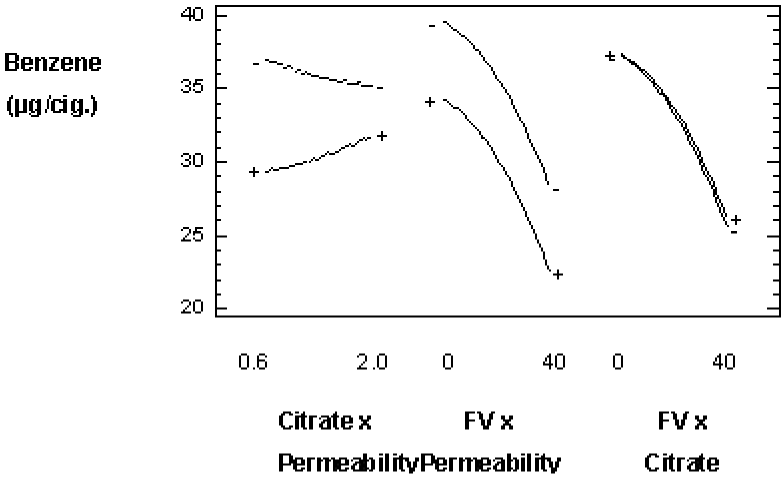
This chart shows the influence of each parameter on benzene. A: paper porosity, B: citrate, C: filter ventilation. Filter ventilation and paper porosity are the main factors decreasing benzene. Citrate has no significant influence. The influence of filter ventilation is quadratic as CC is a significant factor, but can be neglected compared to the main effect C. There is also a significant interaction between permeability and citrate: AB.

Plot of the main effects



Here we can see that when paper permeability is increased from 20 to 80 Coresta, Benzene is reduced from 35 to 30 µg, a decrease of around 15% but depending on the level of citrate as the Pareto chart shows a significant interaction with citrate. Citrate has no influence.
The quadratic effect of ventilation is limited and simplified to a linear influence: 30% decrease when ventilation increases from 0 to 40 %.

Interaction plot of Benzene



The interaction plot show that the interaction between citrate and permeability is qualitative: the influence of paper permeability is significantly higher at 0,6% citrate than at 2%, about

2.5 times more. The two others interactions are not significant as previously seen on the Pareto chart.

Prediction tools: Classification in groups of analytes:

The analyse of each analyte using all these information led to two initial conclusions:

- It is practically very difficult to classify all the analytes in groups of prediction: if we can make groups having, for instance, the same influence of filter ventilation, the analytes in the same group will not follow the same trend for citrate or paper permeability.
- For most of the Hoffmann analytes the effect of filter ventilation, permeability and citrate are not linear, and are complicated by interactions and quadratic effects.

Effect of filter ventilation, paper permeability, and amount of citrate in cigarette paper on the Hoffmann analytes:

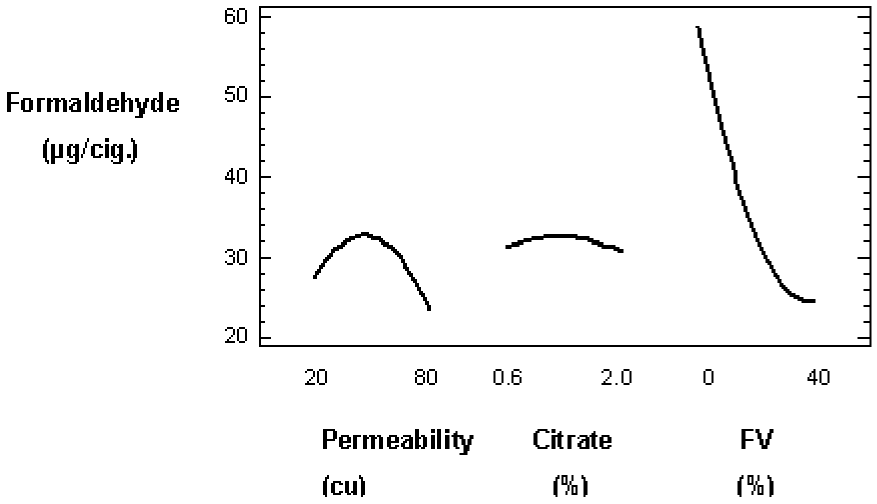
In the table below the influence of each parameter on the analytes are shown.

To make this table we have either used the linear relationships between the parameters and each analyte, and, if not, simplify to linear relationships when the quadratics effects and the interactions between the parameters had little influence on the results. When their influence could not be neglected, the interactions or the quadratic effect are shown.

	Effect of permeability From 20 to 80 cu	**Effect of citrate From 0.6 to 2.0 %**	**Effect of FV From 0 to 40 %**
Tar	~ 15 %	~ 5 %	~ 35 %
Nicotine	~ 10 %	~ 10 %	~ 25 %
CO	15 – 30 % Int. Perm × Cit+ Int . Perm × FV	0 – 15 % Int. Cit × Perm	~ 40 %
Isoprene	~ 15 %	~ 10 %	~ 45 %
NO	5 – 30 % Int. Perm × FV+ Perm × Cit	No effect	25 – 40 % Int. FV × Perm
Acrylonitrile	10 – 30 % Int. Perm × FV	No effect	~ 40 %
Benzene	10 – 25 % Int. Perm × Cit	No effect	~ 30 %
Toluene	5 – 25 % Int. Perm × Cit	No effect	~ 35 %
Total Carbonyls	Quadratic effect Int. Perm × FV	No effect	~ 55 %
Total PAHs	10 – 20 % Int. Perm × Cit	5 – 15 % Int. Cit × Perm	~ 20 %
Total TSNAs	Quadratic effect Int. Perm × FV	Quadratic effect	15 – 30 % Int. FV × Perm

Specific case of the formaldehyde:

One surprising effect which we found in our matrix study was the influence of paper permeability on formaldehyde, and, but to a lesser extent, on the other carbonyls.



What the matrix shows is a very strong influence of filter ventilation with a decrease of 60% from 0 to 40% ventilation, and a maximum of formaldehyde at about 50 Coresta paper permeability.

We rechecked the influence of paper permeability between 20 and 80 Coresta, and we found a different result: formaldehyde stayed constant from 20 to 50 Coresta, and then decreased.

Both results (increase of formaldehyde between 20 and 50 Coresta and then decrease, or no change between 20 and 50 Coresta and then decrease), plus the strong influence of filter ventilation lead to the same conclusion: the cigarette paper real porosity increases formaldehyde formation, which is counterbalanced by the increasing dilution through the cigarette paper when increasing paper permeability.

To minimize formaldehyde it is thus better to use higher porosity cigarette papers.

Conclusion

Our experimental design allows prediction models for most of the Hoffmann analytes, except when the R^2 of the plot between predicted values against obtained was too low, principally because of analytical variations.

The classification of the analytes in groups following the same trend for filter ventilation, citrate and permeability changes is difficult, but reliable trends allowing predictions from the major changes in design, which are filter ventilation and cigarette paper design, are shown:

- The filter ventilation has the main impact to reduce the analytes (from 20 to 40% reduction for 40% added ventilation). It allows, in most cases, direct predictions.
- Cigarette paper permeability has a lower influence (10 to 20 % reduction between 20 and 80 Coresta. Quadratic effects and interactions between the parameters often complicate predictions.
- The level of citrate has little influence between 0.6 and 2.0 %, except in few cases.

Endnotes

1 (Popup - Popup)

Coresta meeting, Freiburg, 7-11 September 2003: “Influence of cigarette paper porosity and citrate content, and of filter ventilation on the Hoffmann analytes”, Jean-Marie Loureau, Jean-Paul Biesse, Grégory Clarisse, Bernard Vidal, Christophe Le Moigne, Stéphane Deberly, Gilles Le-Bourvellec.