# Influence of cigarette paper and filter ventilation on Hoffmann analytes

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## Matrix study on the influence on Hoffmann analytes, 3 parameters :

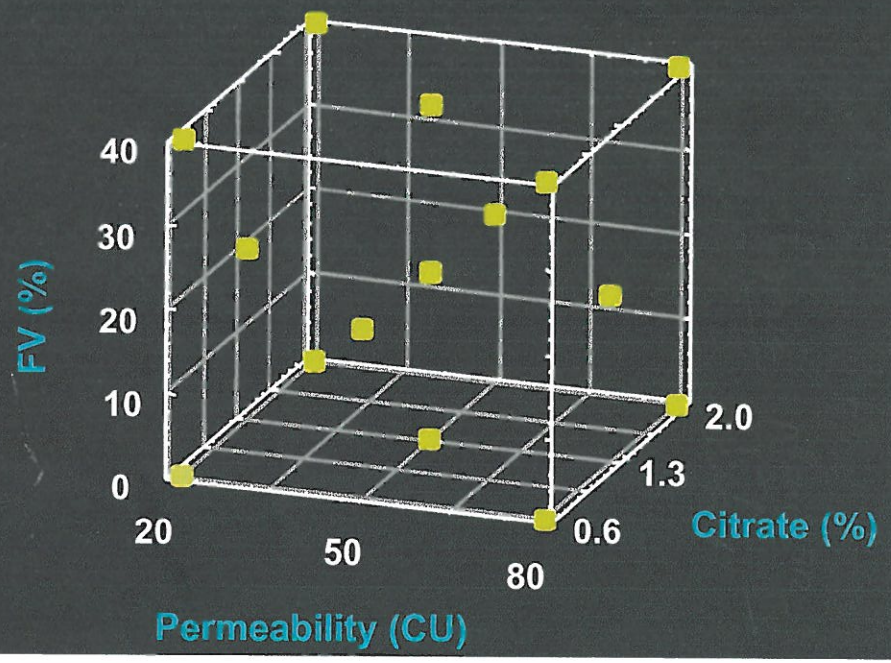
- Filter ventilation (FV)
- Cigarette paper permeability
- Cigarette paper amount of Na/K citrate

## 17 trials

## 3 repetitions at the center point

$$Y = a_0 + a_i X_i + a_{ij} X_i X_j + a_{ii} X^2_i$$

| | Permeability (CU) | Citrate (%) | FV (%) |
|---|---|---|---|
| Level –1 | 20 | 0.6 | 0 |
| Level 0 | 50 | 1.3 | 20 |
| Level +1 | 80 | 2.0 | 40 |



## g size cigarettes, standard American blend

## ffmann 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

| Analyte | CV % |
|---|---|
| TAR | 3 |
| CO | 3.1 |
| Nicotine | 3.4 |
| NO | 3.8 |
| Benzene | 3.9 |
| Total PAH | 4.6 |
| Benzo[a]pyrene | 4.7 |
| EMK | 4.9 |
| Total TSNA | 4.9 |

| Analyte | CV % |
|---|---|
| NAT | 5.1 |
| Benzo[b]fluoranthene | 5.2 |
| Quinoline | 5.4 |
| Chrysene | 5.5 |
| Indeno(123-cd)pyrene | 5.5 |
| Benzo[e]pyrene | 5.6 |
| NNN | 5.6 |
| Fluoranthene | 5.8 |
| Benz[a]anthracene | 5.9 |
| Benzo[k]fluoanthene | 5.9 |
| Pyrene | 5.9 |
| Toluene | 6.1 |
| Acrylonitrile | 6.1 |
| Phenanthrene | 7.2 |
| Butyraldehyde | 7.4 |
| Benzo[ghi]perylene | 7.6 |
| Catechol | 7.7 |
| Propionaldehyde | 7.9 |
| Mercury | 7.9 |
| NNK | 8.1 |
| Acetone | 8.4 |
| Pyridine | 8.5 |
| pH | 8.6 |
| Anthracene | 8.6 |
| Hydroquinone | 8.9 |
| m-,p- Cresol | 9.0 |

| Analyte | CV % |
|---|---|
| NAB | 10.4 |
| Resorcinol | 10.5 |
| Phenol | 10.8 |
| Isoprene | 10.9 |
| Crotonaldehyde | 11.1 |
| NH3 | 12.8 |
| Formaldehyde | 13.2 |
| Total metals | 14.0 |
| Acrolein | 14.1 |
| 1.3-Butadiene | 15.2 |
| Styrene | 16.1 |
| Cadmium | 16.7 |
| HCN | 17.6 |
| Nickel | 18.4 |
| 2-Aminonaphtalene | 23.3 |
| 1-Aminonaphtalene | 25.1 |
| 3-Aminobiphenyl | 25.4 |
| 4-Aminobiphenyl | 25.5 |
| Lead | 25.6 |
| Arsenic | 32.5 |
| Dibenz(ah)anthracene | n.d. |
| Chromium | n.d. |
| Selenium | n.d. |

| | $R^2$ adjusted % |
|---|---|
| CO | 98.2 |
| TAR | 96.7 |
| EMK | 94.5 |
| NO | 94.4 |
| ene | 93.7 |
| tine | 93 |
| yde | 92.8 |
| nyls | 92.3 |
| trile | 91.8 |
| yde | 91.5 |
| yde | 91.3 |
| yde | 91.1 |

| Analyte | $R^2$ adjusted % |
|---|---|
| Pyridine | 88.9 |
| Cadmium | 88.9 |
| Propionaldehyde | 88.9 |
| Acetone | 88.8 |
| Total TSNA | 87.6 |
| Toluene | 87.2 |
| Benzo[b]fluoranthene | 86.8 |
| Total PAH | 86.6 |
| Resorcinol | 86.5 |
| NNN | 86.1 |
| Acrolein | 85.6 |
| HCN | 85.5 |
| Indeno(123-cd)pyrene | 85.4 |
| Benzo[a]pyrene | 85.2 |
| NAT | 83.4 |
| Benzo[e]pyrene | 81.4 |
| Total metals | 81.3 |
| Styrene | 81.0 |
| Benz[a]anthracene | 80.7 |
| Benzo[k]fluoanthene | 80.2 |

| Analyte | $R^2$ adju |
|---|---|
| Isoprene | 79 |
| NAB | 79 |
| Fluoranthrene | 78 |
| Benzo[ghi]perylene | 78 |
| Phenanthrene | 75 |
| Quinoline | 75 |
| NNK | 74 |
| Mercury | 73 |
| Pyrene | 72 |
| Chrysene | 70 |
| 1.3-Butadiene | 69 |
| Anthracene | 68 |
| Lead | 68 |
| Catechol | 68 |
| NH3 | 67 |
| Hydroquinone | 66 |
| Phenol | 55 |
| Arsenic | 51 |
| m-,p- Cresol | 50 |
| o-Cresol | 48 |
| Nickel | 46 |
| 4-Aminobiphenyl | 21 |
| 3-Aminobiphenyl | 21 |
| 2-Aminonaphtalene | 9 |
| 1-Aminonaphtalene | 4 |

**Based on low adjusted $R^2$ data and on high analytical coefficient of variation, some Hoffmann analytes could not be predicted :**

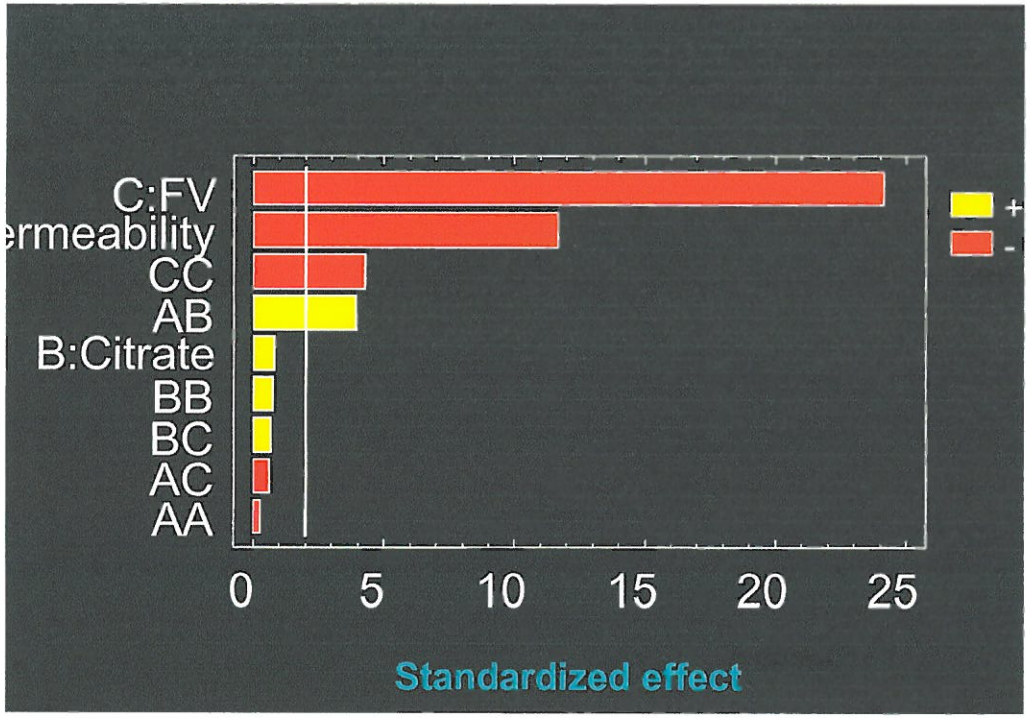
- Metals
- Aromatic amines
- Ammonia
- HCN
- Phenolic compounds

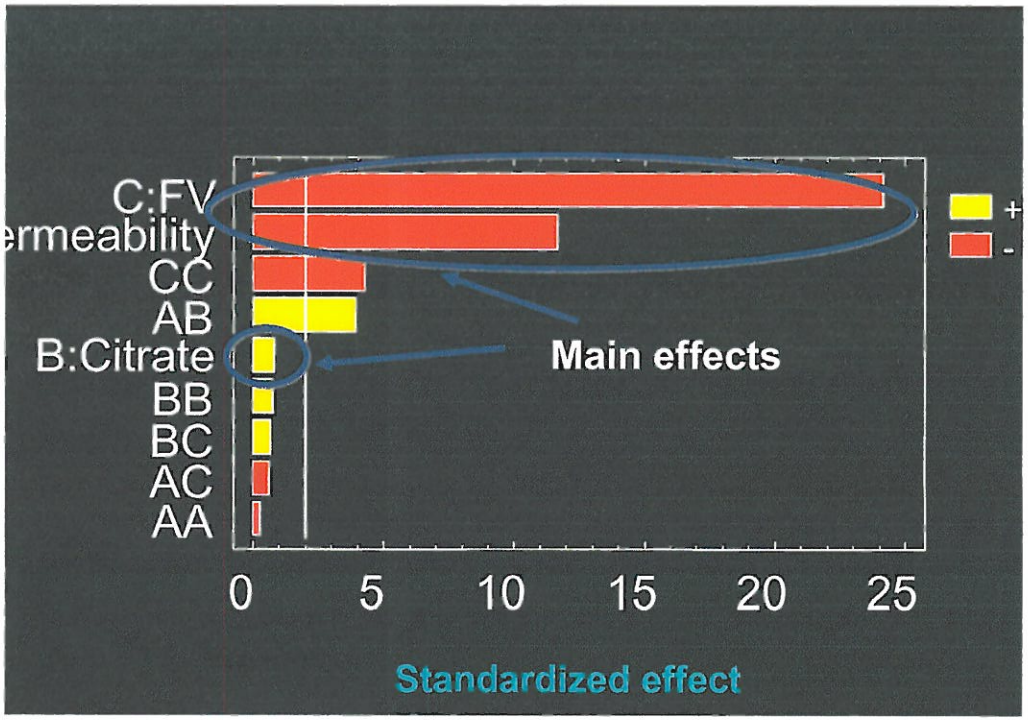
## Based on better adjusted $R^2$ and lower coefficient of variation, we could establish prediction models for :

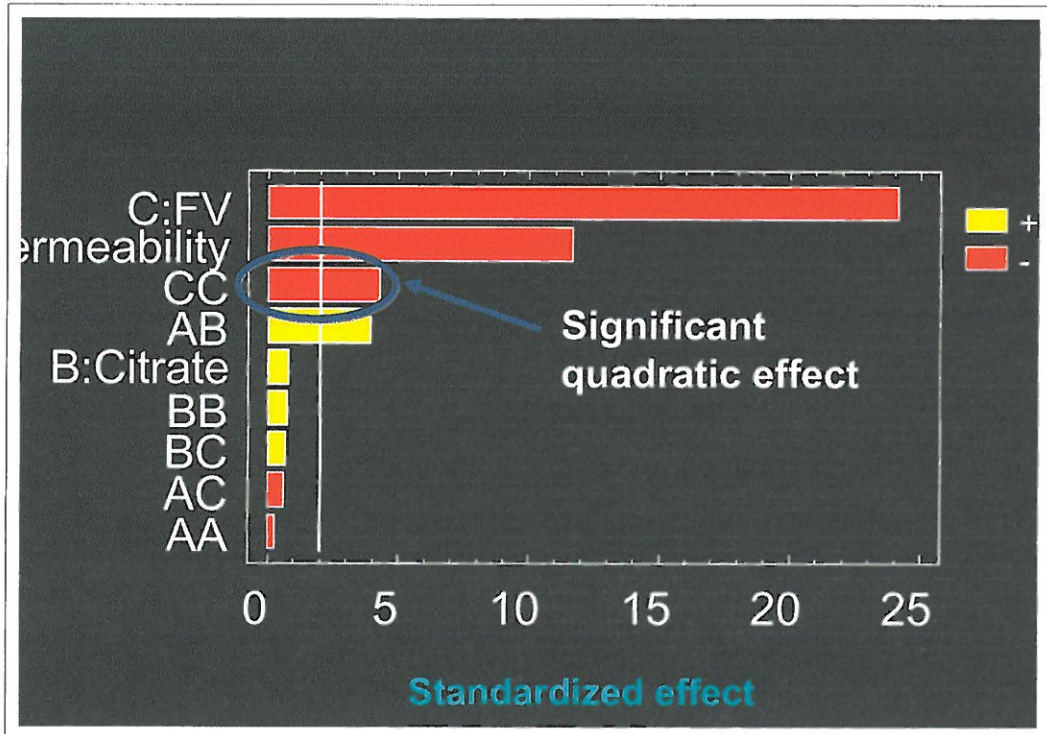
- Tar
- Nicotine
- CO
- NO
- PAH
- TSNA
- Carbonyls
- Volatiles and semi volatiles

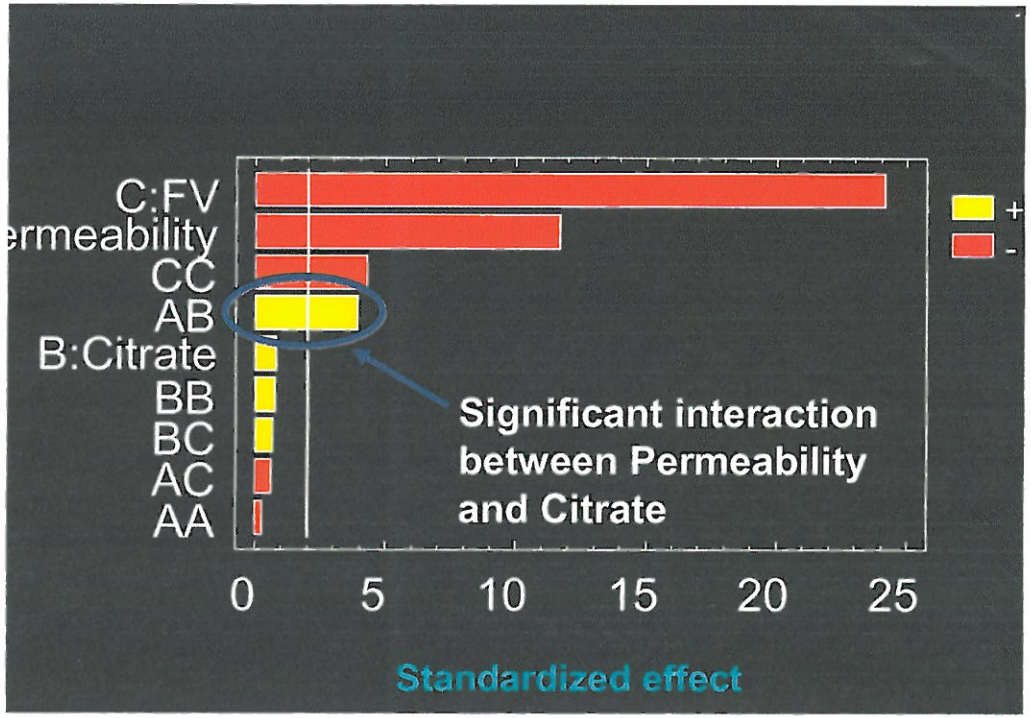
## Benzene

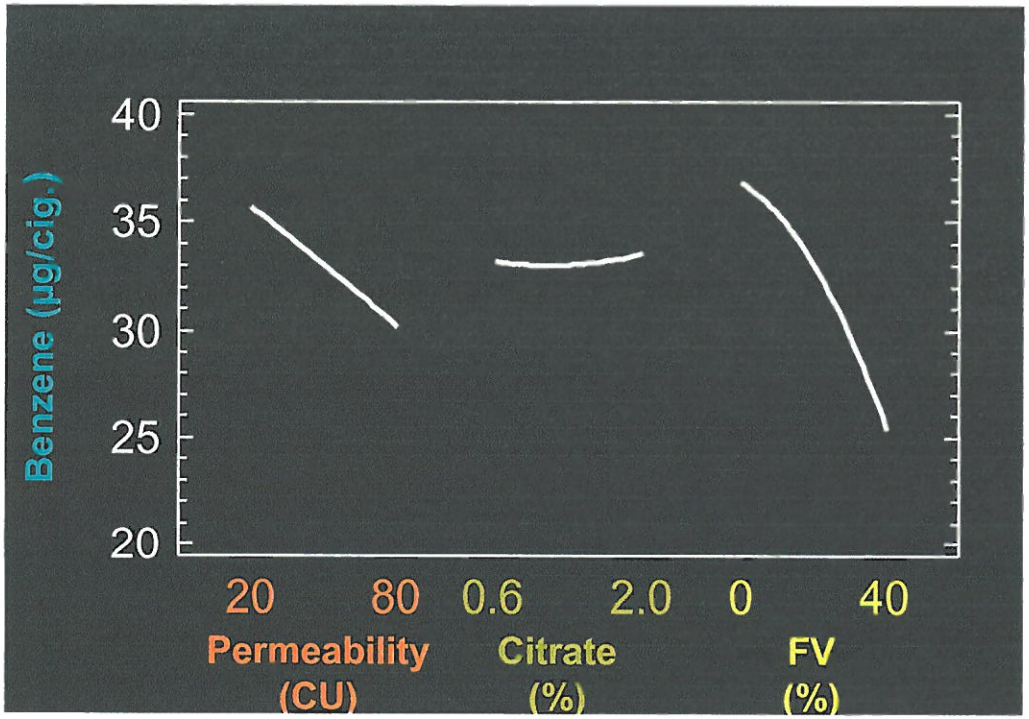
## Statistical analysis and prediction mod

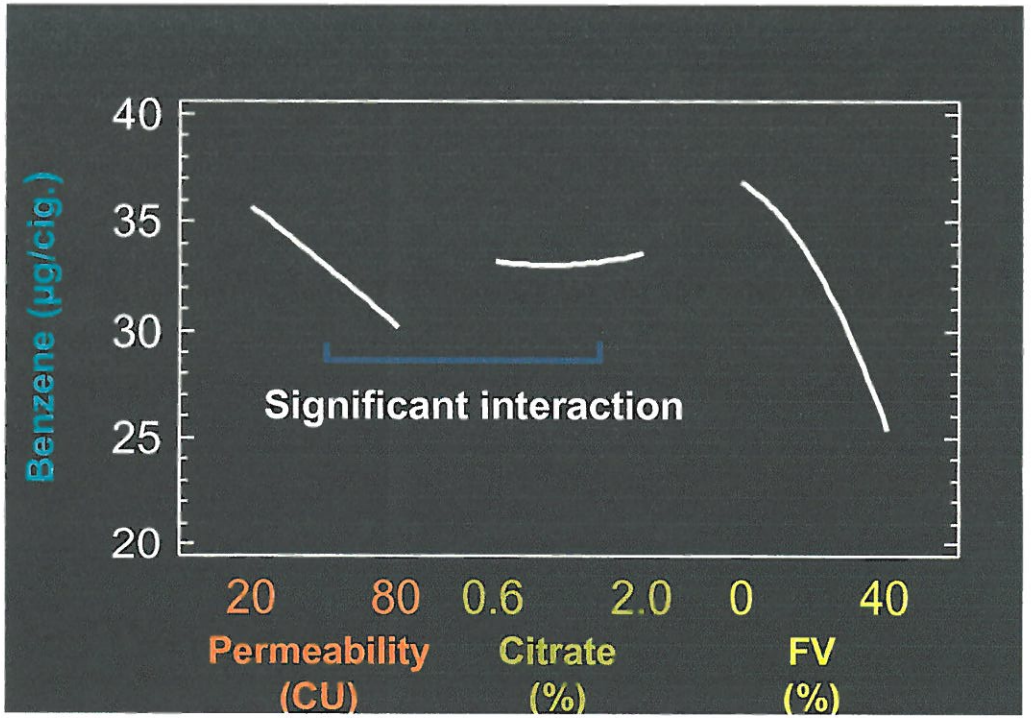



C:FV
ermeability
CC
AB
B:Citrate
BB
BC
AC
AA
+
-
Significant
quadratic effect
0
5
10
15
20
25
Standardized effect


C:FV
ermeability
CC
AB
B:Citrate
BB
BC
AC
AA
+
-
Significant interaction
between Permeability
and Citrate
0
5
10
15
20
25
Standardized effect


Benzene (µg/cig.)
40
35
30
25
20
20
80
Permeability
(CU)
0.6
2.0
Citrate
(%)
0
40
FV
(%)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Citrate
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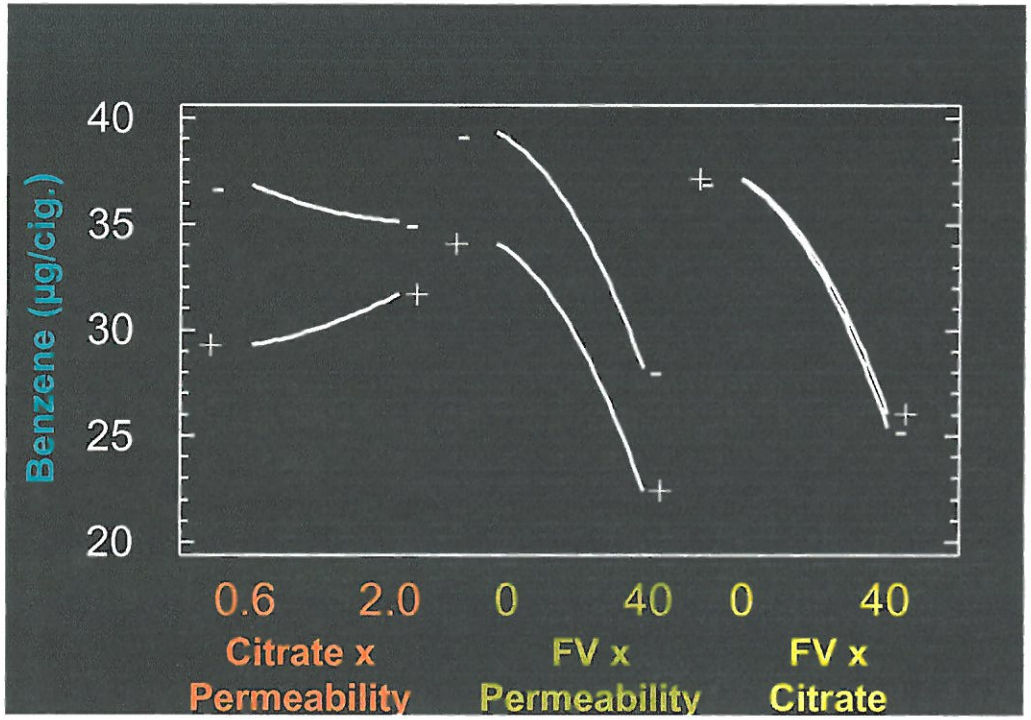
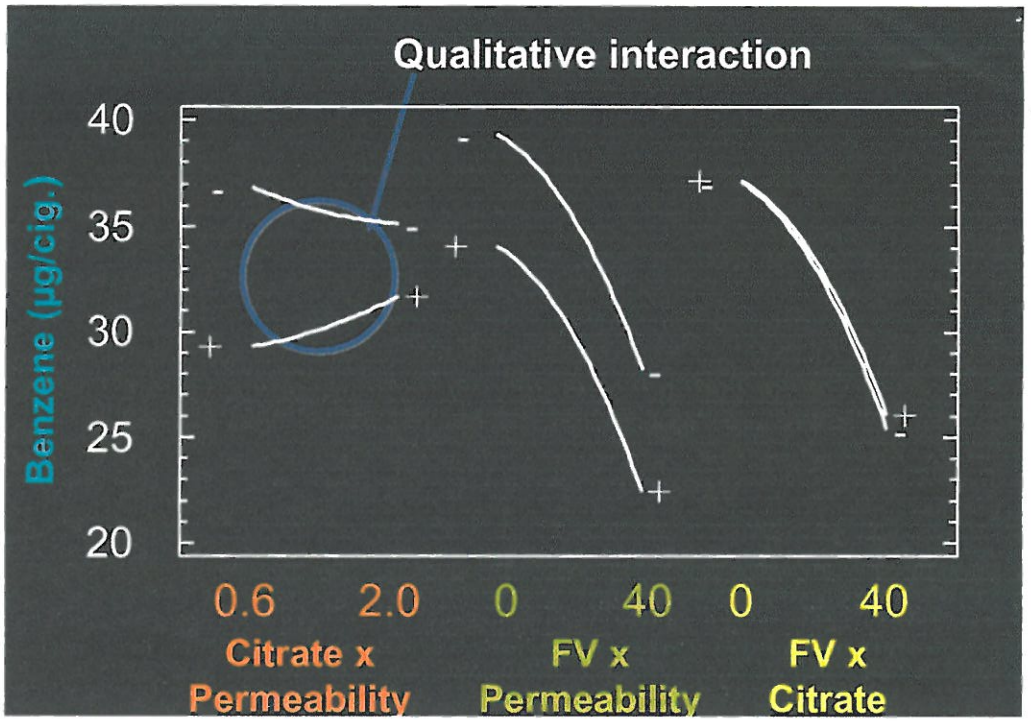
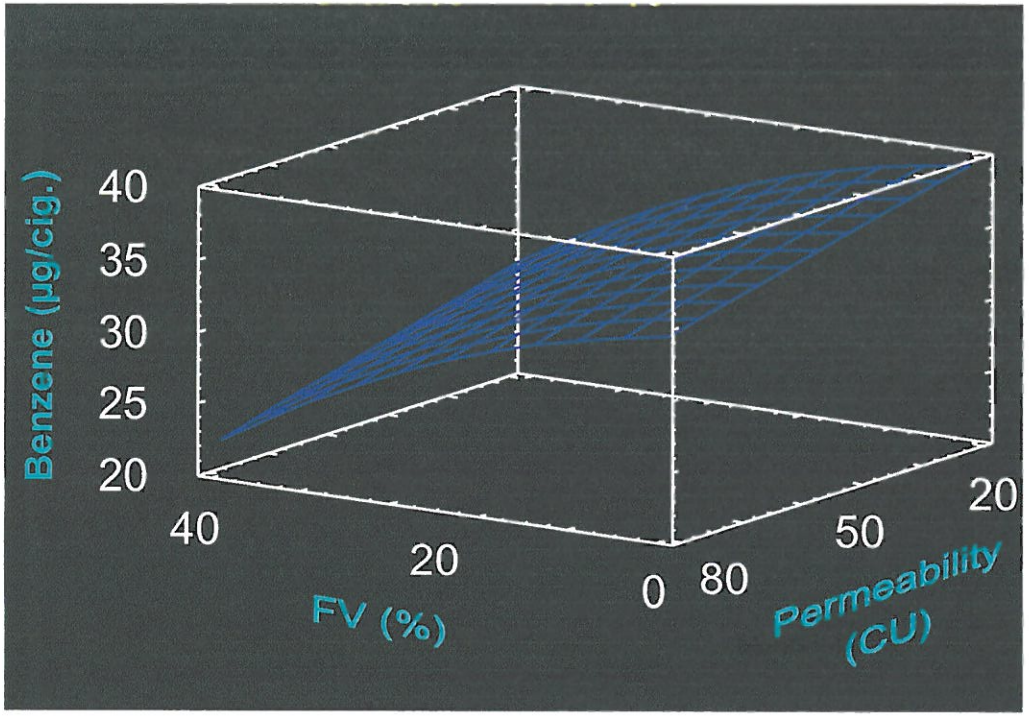
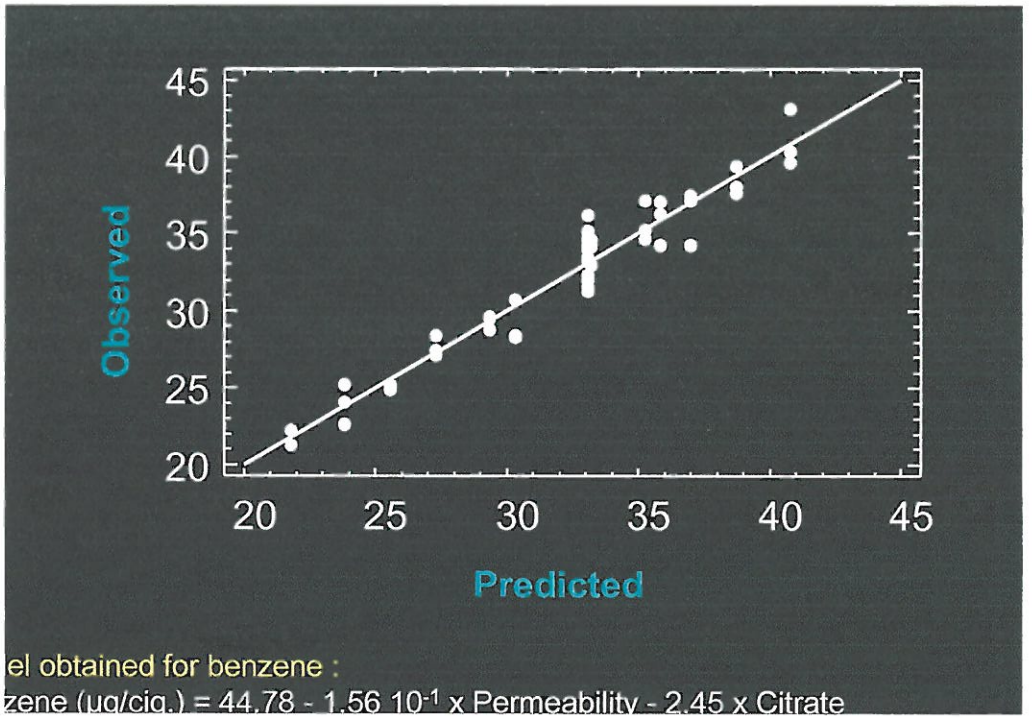
FV
(%)




el obtained for benzene :

zene (µg/cig.) = 44.78 - 1.56 $10^{-1}$ x Permeability - 2.45 x Citrate

g)

$$Tar = 13.38 - 4.88\ 10^{-2} \times Permeability - 2.54\ 10^{-1} \times Citrate - 6.09\ 10^{-2} \times FV + 2.27\ 10^{-4} \times Permeability^2 - 7.77\ 10^{-4} \times FV^2$$

$R^2 = 96.7\ \%$

ne
g)

$$Nicotine = 1.18 - 4.87\ 10^{-3} \times Permeability - 8.12\ 10^{-2} \times Citrate - 3.49\ 10^{-3} \times FV + 3.25.10^{-5} \times Permeability^2 + 1.01\ 10^{-3} \times Citrate \times FV - 8.94.10^{-5} \times FV^2$$

$R^2 = 93.0\ \%$

g)

$$CO = 21.25 - 1.37\ 10^{-1} \times Permeability - 2.84 \times Citrate - 1.22\ 10^{-1} \times + 6.10\ 10^{-4} \times Permeability^2 + 1.69\ 10^{-2} \times Permeability \times Citrate + 2.85\ 10^{-4} \times Permeability \times FV + 5.09\ 10^{-1} \times Citrate^2 - 1.09\ 10^{-3} \times$$

$R^2 = 98.2\ \%$

Ranges : Permeability [20 – 80 CU]

## al : to estimate independently the effect of the 3 ameters filter ventilation, cigarette paper meability and citrate level on Hoffmann analytes l to focus only on linear relationships

- This is possible only when there is no significant interactions between the studied parameter and the 2 others
- And when there is no quadratic effect for the studied parameter

| Hoffmann analytes | Yield reduction |
|---|---|
| Tar<br>Isoprene | ~ 15 % |
| Nicotine | ~ 10 % |

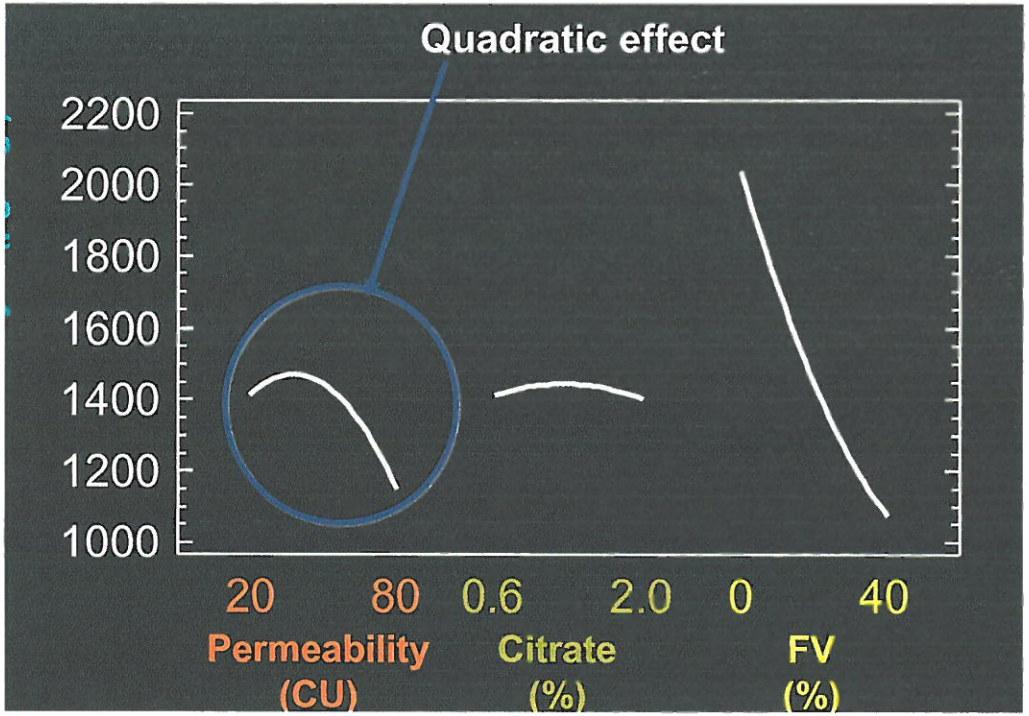
| Hoffmann analytes | Yield reduction |
|---|---|
| Nicotine<br>Isoprene | ~ 10 % |
| Tar | ~ 5 % |
| NO<br>Acrylonitrile<br>Benzene<br>Toluene<br>Total Carbonyls | Not significant |

| Hoffmann analytes | Yield reduction |
|---|---|
| Total carbonyls | ~ 55 %<br>~ 1.40 x FV |
| Isoprene<br>CO<br>Acrylonitrile | 35 % - 45 %<br>[0.90 x VF] - [1.15 x FV |
| Tar<br>Benzene<br>Toluene | 30 % - 35 %<br>[0.75 x FV] - [0.90 x FV |
| Nicotine<br>Total PAHs | 20 % - 30 %<br>[0.50 x FV] - [0.75 x FV |

most of the Hoffmann analytes the effects
permeability and citrate are not direct and are
mplicated by interactions and / or quadratic effe

can categorize the effects as follows :

* No effect
* Linear effect
* Interactions between parameters
* Quadratic effect




| | Effect of permeability from 20 to 80 CU | Effect of citrate from 0.6 to 2.0 % | Effe of F from 0 t |
|---|---|---|---|
| r | ~ 15 % | ~ 5 % | ~ 35 |
| tine | ~ 10 % | ~ 10 % | ~ 25 |
| D | 15 - 30 %<br>Int. Perm x Cit<br>+ Int. Perm x FV | 0 - 15 %<br>Int. Cit x Perm | ~ 40 |
| ene | ~ 15 % | ~ 10 % | ~ 45 |

| | Effect of permeability from 20 to 80 CU | Effect of citrate from 0.6 to 2.0 % | Effe of F from 0 t |
|---|---|---|---|
| D | 5 - 30 %<br>Int. Perm x FV<br>+ Perm x Cit | No effect | 25 - 40<br>Int. FV x F |
| lonitrile | 10 – 30 %<br>Int. Perm x FV | No effect | ~ 40 |
| nzene | 10 – 25 %<br>Int. Perm x Cit | No effect | ~ 30 |
| luene | 5 – 25 %<br>Int. Perm x Cit | No effect | ~ 35 |

| | Effect of permeability from 20 to 80 CU | Effect of citrate from 0.6 to 2.0 % | Effe of F from 0 t |
|---|---|---|---|
| tal onyls | Quadratic effect<br>+ Int. Perm x FV | No effect | ~ 55 |
| tal Hs | 10 – 20 %<br>Int. Perm x Cit | 5 – 15 %<br>Int. Cit x Perm | ~ 20 |
| tal As | Quadratic effect<br>+ Int. Perm x FV | Quadratic effect | 15 - 30<br>Int. FV x F |

ne scope of our experimental design :

diction models could be established for most of the ffmann analytes except when $R^2$ and analytical CoV e not acceptable

classification of Hoffmann analytes in groups followi ne trends for filter ventilation and citrate and permeab nges is difficult

ne scope of our experimental design, we have present ds which are useful for the cigarette design :

filter ventilation has a main impact to reduce Hoffma lytes (from 20 to 60 % reduction for 40% dilution incre lows, in most cases direct predictions

arette paper permeability has a lower influence, (10 to ween 20 and 80 CU), predictions are often complicate dratic effect and interactions with the other parameter

level of citrate has little influence between 0.6 and 2.0 ept in few cases

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