Mechanisms of transfer of ammonia in smoke from ammonium compounds in tobacco

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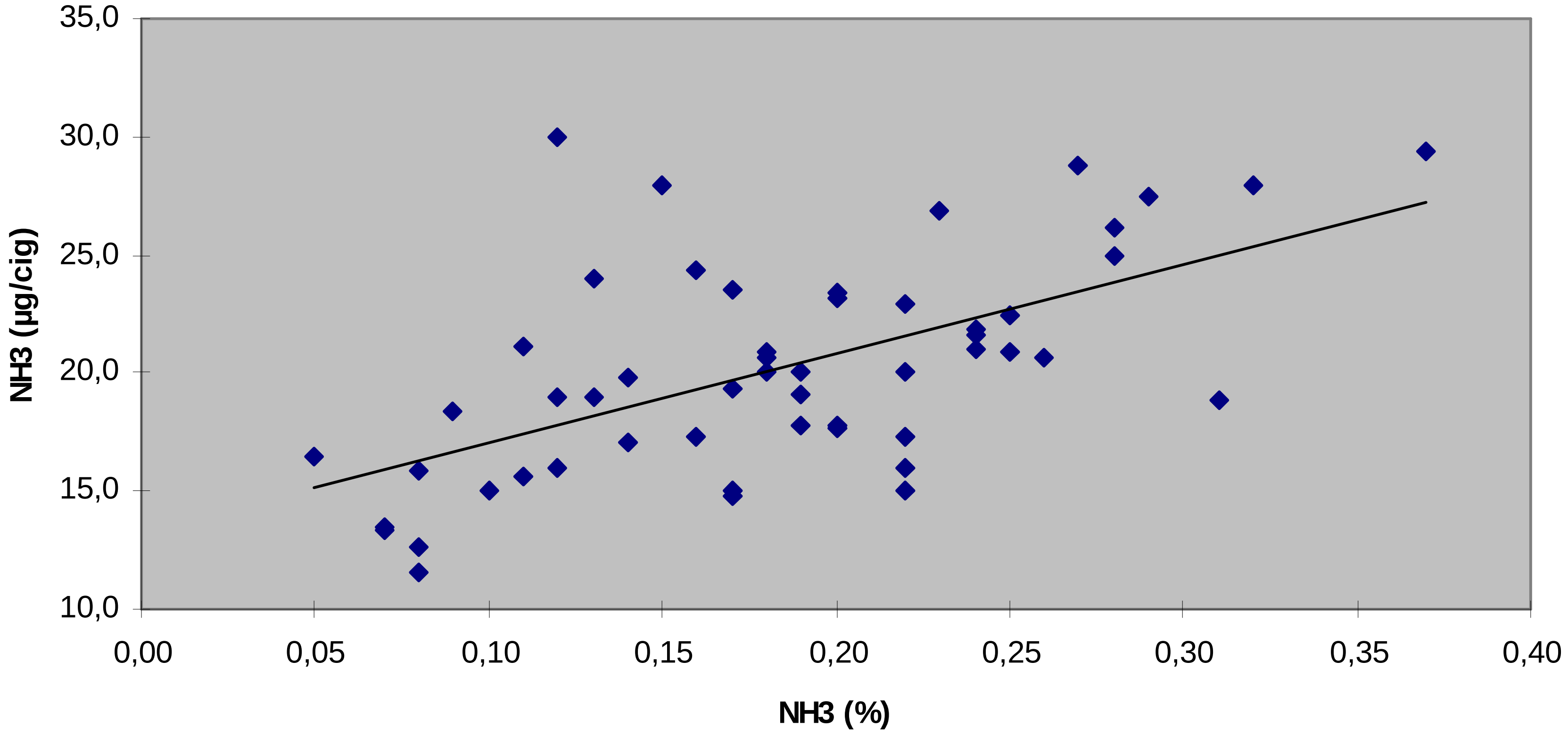
European Tobacco Company

Survey of the European market (1998)

- 53 leading brands in Europe
  - France (24), Netherlands, Belgium, Germany, Italy, Spain, Switzerland, Austria, Greece and UK
  - Exclusively Virginia and American blends
  - Full flavor (tar between 10 and 15 mg)
- Survey of different chemical and physical parameters
  - Ammonium in tobacco, Ammonia in smoke

Relationship between Ammonium in Tobacco and Ammonia in smoke



Relationship between Ammonium in Tobacco and Ammonia in smoke

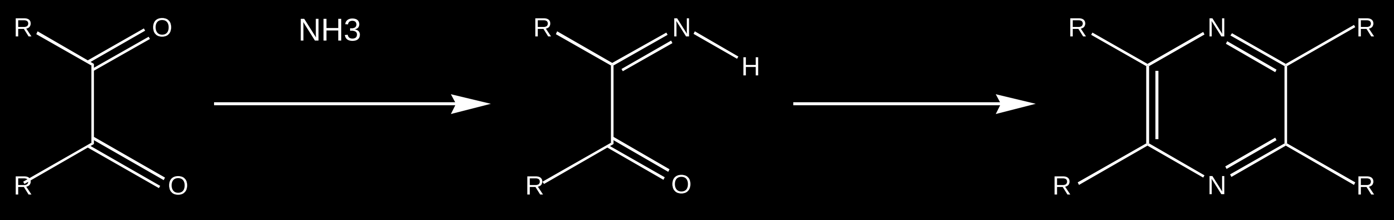
- Linear regression
  - $NH_3 = 13.2 + 37.9\ NH_4$
    - NH_3 in µg/cig
    - NH_4 in % in dry tobacco
  - $r = 0.594$;
  - ANOVA : $p < 0.01$; significant relationship
- Interpretation of results difficult because
  - differences in blend and cigarette design

Transfer of Ammonia From Ammonium compounds

- These data seem to illustrate a direct transfer of Ammonia into smoke from Ammonium compounds in tobacco with a very low transfer rate
    - An increase of 0.2 % of Ammonium in blend
    - gives a mean increase of **8 µg / cig** of ammonia
        - from the regression equation
    - with a potential of **130 µg / cig**
        - assuming 800 mg of tobacco /cig
        - and a transfer rate of 8 % (equivalent to nicotine)

Experimental design

- Hypotheses
  - Ammonium compounds produce Ammonia under thermal degradation
  - Ammonia reacts with carbonyl compounds produced by the pyrolysis of carbohydrates
    - with a special emphasis on sugars (Glucose, Fructose and Sucrose which degradation occurs at the same temperature range)



Experimental design
Response surface type

- American blend
  - Addition of controlled amounts of DAP and Sucrose

		DAP		
		0 %	**1 %**	**2 %**
	0 %	S1D1	S1D2	S1D3
Sucrose	**2,5 %**	S2D1	S2D2	S2D3
	5 %	S3D1	S3D2	S3D3

  - King size cigarette
    - Constant tobacco weight : 792 mg
    - no filter ventilation

Controlled parameters
Tobacco rod

- Total alkaloïds
- Ammonium
- Glucose, Fructose, Sucrose
- Phosphate
    - Continuous Flow Analysis

Tobacco - Ammonium

	DAP0		DAP1		DAP2	
	m	th	m	th	m	th
S0	0.30	0.30	0.52	0.53	0.72	0.76
S2.5	0.30	0.29	0.52	0.52	0.71	0.75
S5	0.29	0.29	0.49	0.51	0.71	0.73

% in dry tobacco

Tobacco - Sucrose

	DAP0		DAP1		DAP2	
	m	th	m	th	m	th
S0	0.87	0.87	0.80	0.86	0.63	0.85
S2.5	2.67	3.29	2.53	3.26	2.67	3.22
S5	4.75	5.59	4.73	5.54	4.81	5.49

% in dry tobacco

Tobacco - Glucose

	DAP0		DAP1		DAP2	
	m	th	m	th	m	th
S0	1.78	1.78	1.63	1.76	1.55	1.75
S2.5	1.80	1.74	1.73	1.72	1.77	1.70
S5	2.10	1.70	1.92	1.68	1.86	1.66

% in dry tobacco

Same pattern for Fructose

Tobacco - Alcaloïds

	DAP0		DAP1		DAP2	
	m	th	m	th	m	th
S0	2.17	2.17	2.13	2.15	2.13	2.13
S2.5	2.12	2.12	2.06	2.10	2.05	2.08
S5	2.06	2.07	2.04	2.05	2.01	2.03

% in dry tobacco

Tobacco analysis - Conclusions

- The experimental design was realised as planned
- Sucrose was partially inverted to Glucose and Fructose during the process
- Reaction between sugars and DAP may have occurred at this stage

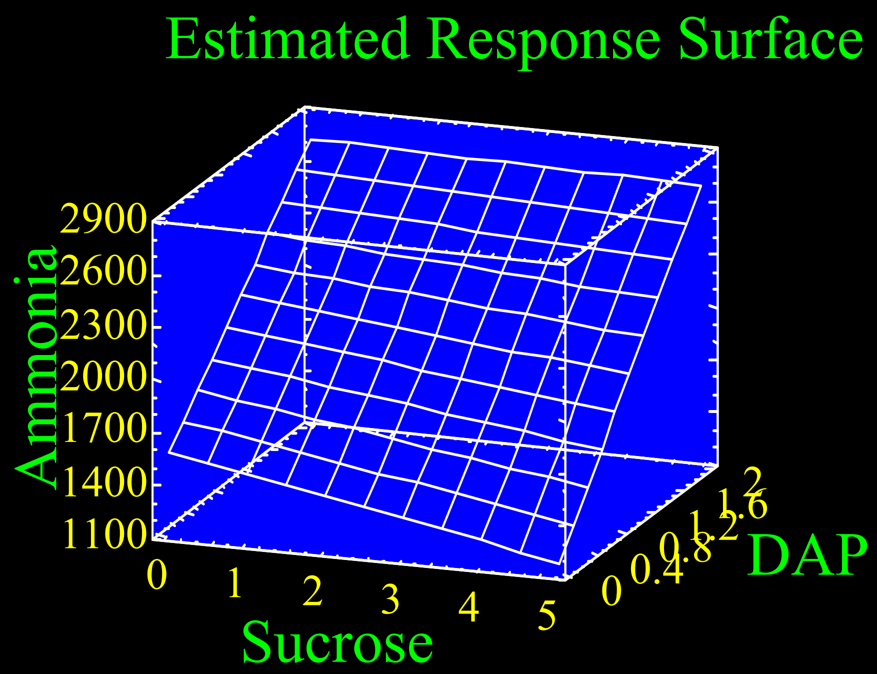
Transfer of Ammonia
Variables

- Smoke
  - Tar, Nicotine
    - ISO methods
  - Pyrazines
    - GC
  - Diacetyl, Methylglyoxal
    - HPLC (derivatization with o plenylendiamine)
  - Ammonia
    - Ion exchange liquid Chromatography

Methodology

- Variables expressed in ppm / NFDPM
- Mathematical model
  - $V = a + b \times A + c \times B + d \times AB + e \times A^2 + f \times B^2$
    - where : A is added sucrose in % and B is added DAP in %
- ANOVA
  - To simplify the model (exclude or not the second order terms in the model)
- Calculate the final model and the estimated response surface

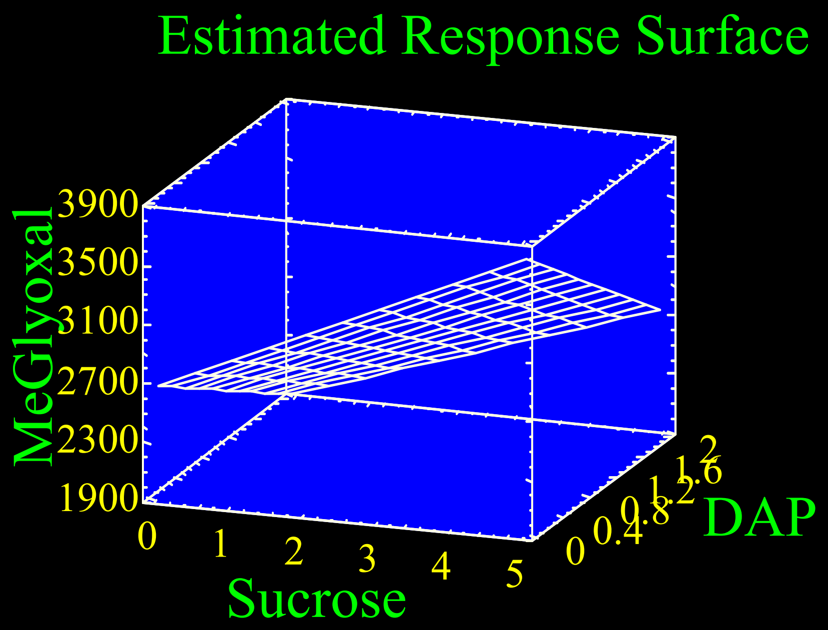
Smoke - Ammonia



R^2 = 0.841

NH3 = 1572.6 - 80 x S + 586.6 x DAP + 36.1 x S x DAP

Smoke - MethylGlyoxal

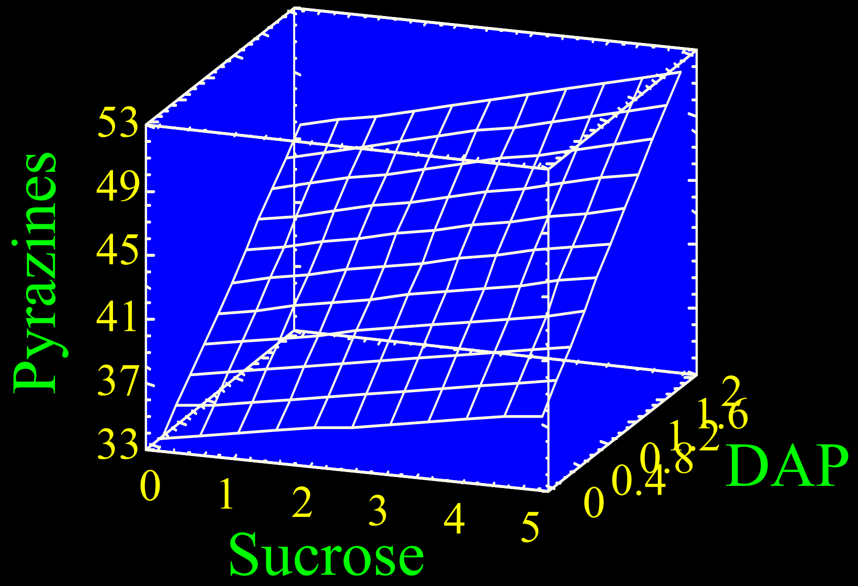


$R^2 = 0.904$

MeG = 2669.3 + 223 X S - 370.1 x DAP - 29.5 x S x DAP

Smoke - Pyrazines

Estimated Response Surface



$R^2 = 0.863$

Pyr = 33.5 + 0.78 x S + 6.2 x DAP + 0.2 x S x DAP

Transfer of ammonia

- There is a direct transfer of ammonia in smoke from ammonium compounds
- This transfer is partially inhibited when sucrose yields increase
- Ammonia reacts with some carbonyl compounds produced by sugar pyrolysis

Effect on Nicotine transfer

Variables

- Nicotine
    - Expressed in % of DTPM
- Nicotine in vapour phase
    - Expressed in % of total Nicotine
    - Denuder tube method
- "Smoke pH"
    - Total smoke
    - Condensate
        - Aqueous solutions

pH - Total smoke

	DAP0	DAP1	DAP2
S0	5,54	5,52	5,64
S2.5	5,51	5,51	5,44
S5	5,46	5,44	5,53

No significant effect

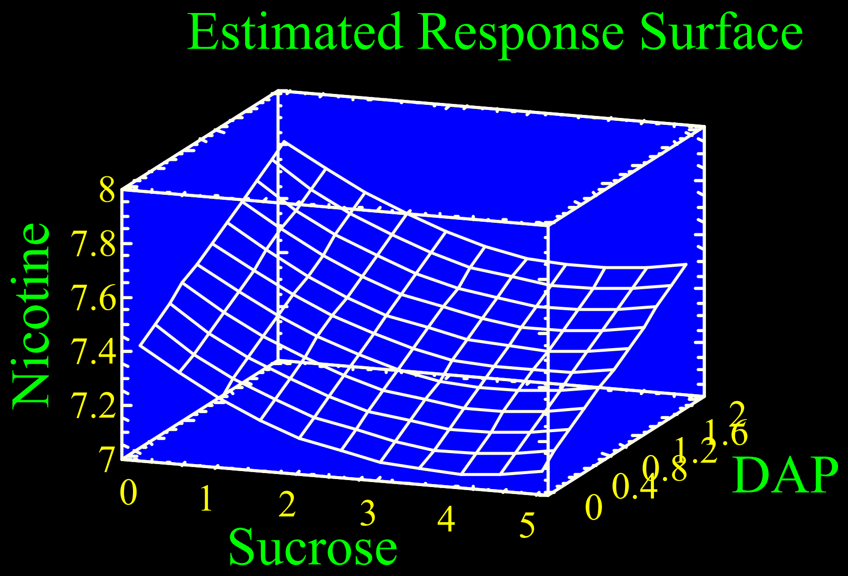
pH - TPM

	DAP0	DAP1	DAP2
S0	6,36	6,27	6,31
S2.5	6,23	6,30	6,24
S5	6,18	6,38	6,26

No significant effect

Nicotine

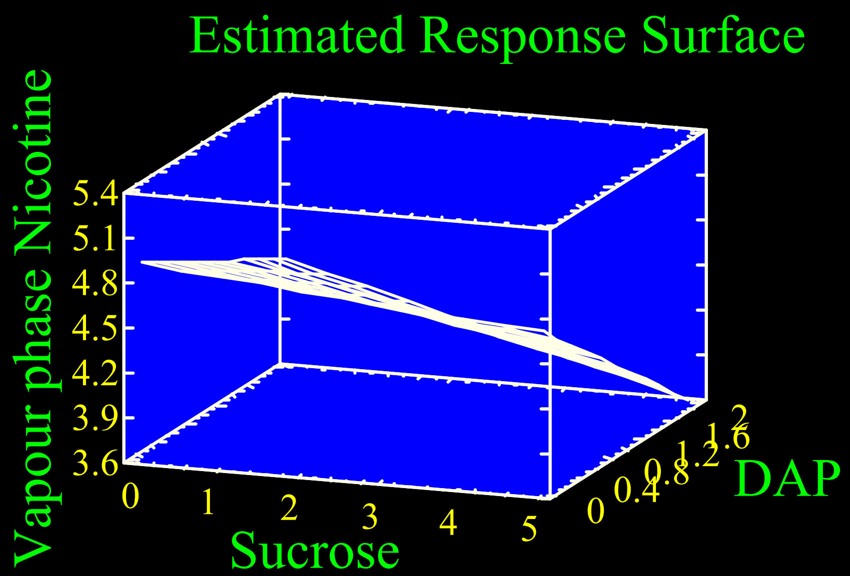
% of Dry PM



$R^2 = 0.824$

$Nic = 7.415 - 0.196 \times S + 0.208 \times DAP + 0.026 \times S^2$

Vapour Phase Nicotine
% of total Nicotine



R^2 = 0.694

VPNic = 4.92 - 0.048 x S - 0.296 DAP - 0.047 x S x DAP

Effect on Nicotine transfer

- No modification of “smoke pH”
  - whatever the trapping method used
- Very limited modification of Nicotine concentration in condensate
  - Combustibility effect ?
- No increase of Nicotine in vapour phase
  - a decrease is observed instead

Summary

- The direct transfer of Ammonia in smoke from Ammonium compounds is probably controlled by the ammonium yield and the sugars (and related compounds) yield
- No significant effect on Nicotine transfer in smoke have been observed