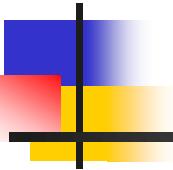
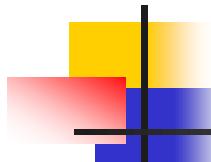


Determination of Harmful Components in Mainstream Cigarette Smoke by FT-NIR Spectrometry Equipped with Cambridge Filter Pads



Zhiguo Wang

Technology Center of China Tobacco Hunan Industrial Co. Ltd



What is the work about?

A fast method for the determination of components in smoke will be introduced

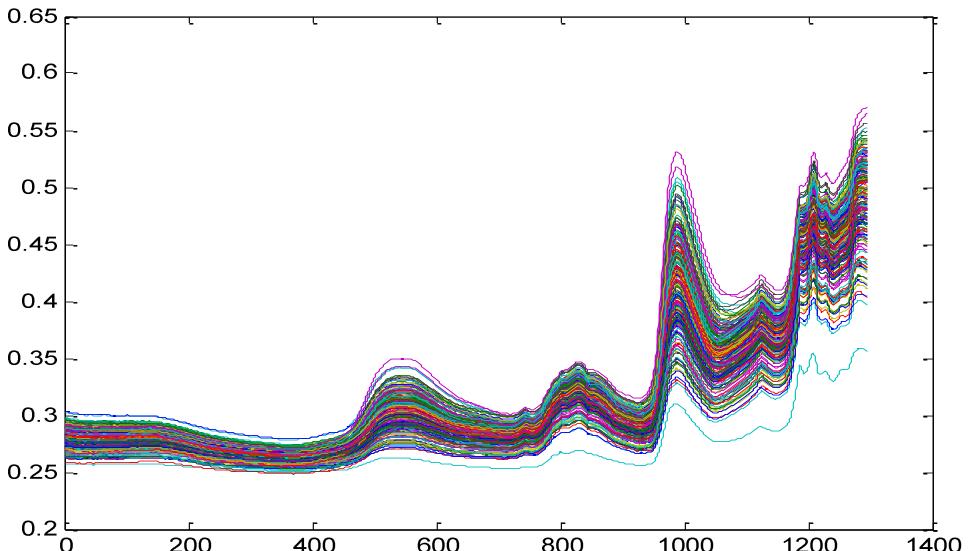
- How fast or how efficiency ?

Several or even more smoke components can be determined in a minute after cigarette smoking

- What is the work used for?

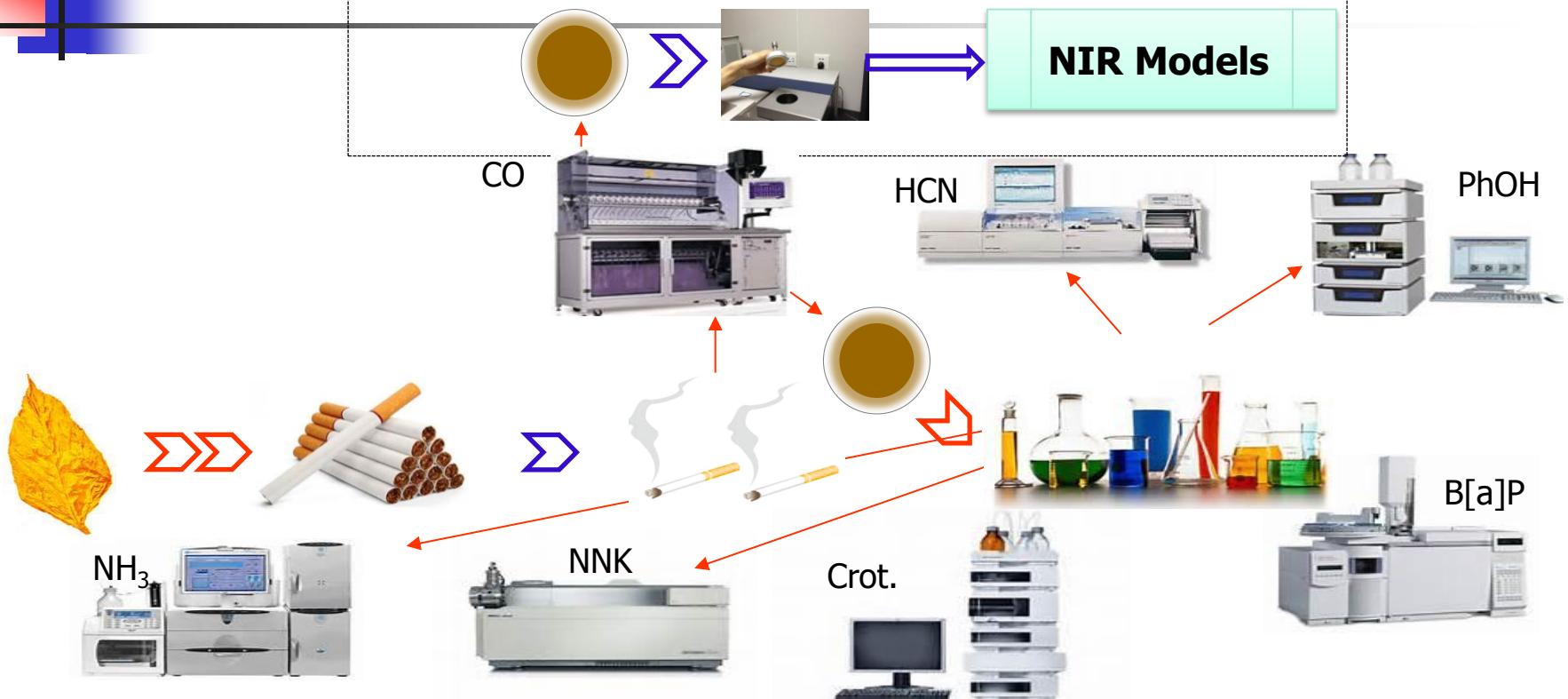
To evaluate and control the cigarette manufacturing variability

FT-NIR spectra of smoke particulate



**NIR spectra contain plenty of chemical information
(-CH, -NH, -OH,,)**

Advantages of the method



Influence of spectra scan on test data

	CO(mg/Cig)		PhOH(ug/cig)		HCN(ug/Cig)		NH3(ug/cig)		BaP(ng/cig)		NNK(ng/Cig)	
	Scan	Unscan	Scan	Unscan	Scan	Unscan	Scan	Unscan	Scan	Unscan	Scan	Unscan
A	12.49	12.56	17.94	17.24	118.48	119.18	6.53	6.59	8.81	8.75	5.69	5.22
B	10.55	10.67	16.50	15.84	77.74	77.20	3.37	3.50	7.10	6.97	3.18	2.91
C	7.39	7.45	11.32	11.28	48.60	49.22	2.09	2.25	5.39	5.36	3.54	2.96
D	11.18	11.10	17.06	16.64	91.92	92.40	8.55	8.73	9.21	9.06	48.88	52.45
E	8.34	8.49	11.10	11.90	66.90	66.18	6.02	6.15	6.54	6.37	37.38	35.10

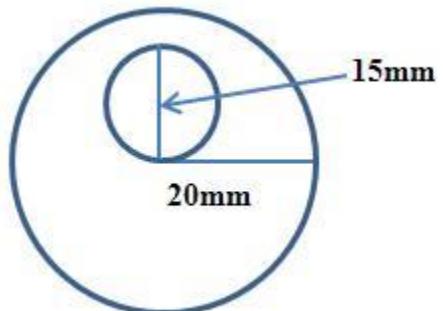
	CO(mg/Cig)		PhOH(ug/cig)		HCN(ug/Cig)		NH3(ug/cig)		BaP(ng/cig)		NNK(ng/Cig)	
	P	H	P	H	P	H	P	H	P	H	P	H
A	0.51	0	0.11	0	0.73	0	0.82	0	0.65	0	0.09	0
B	0.42	0	0.14	0	0.75	0	0.44	0	0.28	0	0.23	0
C	0.33	0	0.92	0	0.63	0	0.37	0	0.64	0	0.04	1
D	0.40	0	0.49	0	0.79	0	0.33	0	0.32	0	0.28	0
E	0.03	1	0.23	0	0.64	0	0.54	0	0.26	0	0.22	0

Distribution of particulate matter

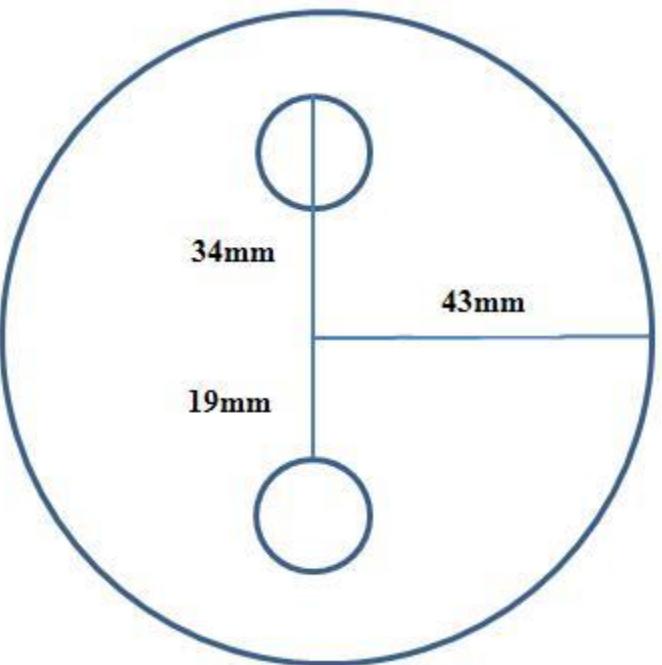
Position	CO	BaP	NNK	HCN	NH3	PhOH	Crot.
1	11.89	7.77	3.71	105.99	8.03	4.62	17.91
2	11.85	8.01	3.58	118.11	8.13	4.61	18.19
3	11.49	7.71	3.49	101.37	7.90	4.56	16.64
4	10.94	7.74	3.38	105.29	7.85	4.34	15.18
5	11.13	7.95	3.27	129.15	7.95	3.79	16.62
6	10.59	7.67	3.24	106.40	7.78	4.62	14.65
7	10.58	7.88	3.15	112.77	7.92	4.15	14.75
8	10.59	8.01	3.05	126.33	7.97	3.56	15.33
9	10.35	7.73	3.09	109.33	7.76	3.97	14.16
10	10.02	7.58	2.99	96.44	7.63	4.29	12.78
Mean	10.94	7.81	3.30	111.12	7.89	4.25	15.62
SD	0.64	0.15	0.24	10.56	0.14	0.38	1.70
CV	5.81	1.91	7.28	9.51	1.82	8.89	10.89



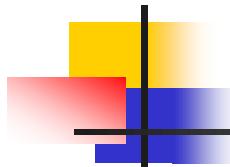
Spectral scanned area



44mm Cambridge filter: 56%



92mm Cambridge filter: 43%



Determination of smoke components

- Tar and TPM: ISO4387
- Nicotine: ISO10315
- CO: ISO8454
- Crotonaldehyde: YC/T254-2008
- PhOH: YC/T255-2008
- HCN: YC/T 253-2008
- NH3: YC/T 377-2010
- B[a]P: GB/T 21130-2007
- NNK: GB/T 23228-2008

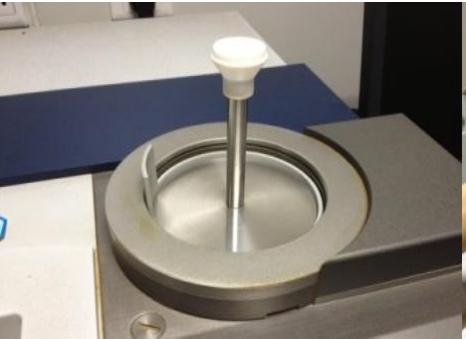
Spectra Scan

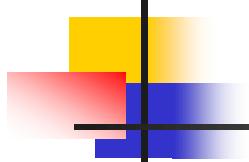
Wavenumber: 9000-4000cm⁻¹

Resolution: 4cm⁻¹

Detector: PbS

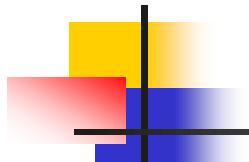
Scan: 64





Program of PLS

- $Y = XB + E$ (1)
- $T = XW$ (2)
- $Y = TP + F$ (3)
- $Y = XWP$ (4)
- $B = WP$ (5)



Parameters for model optimizing

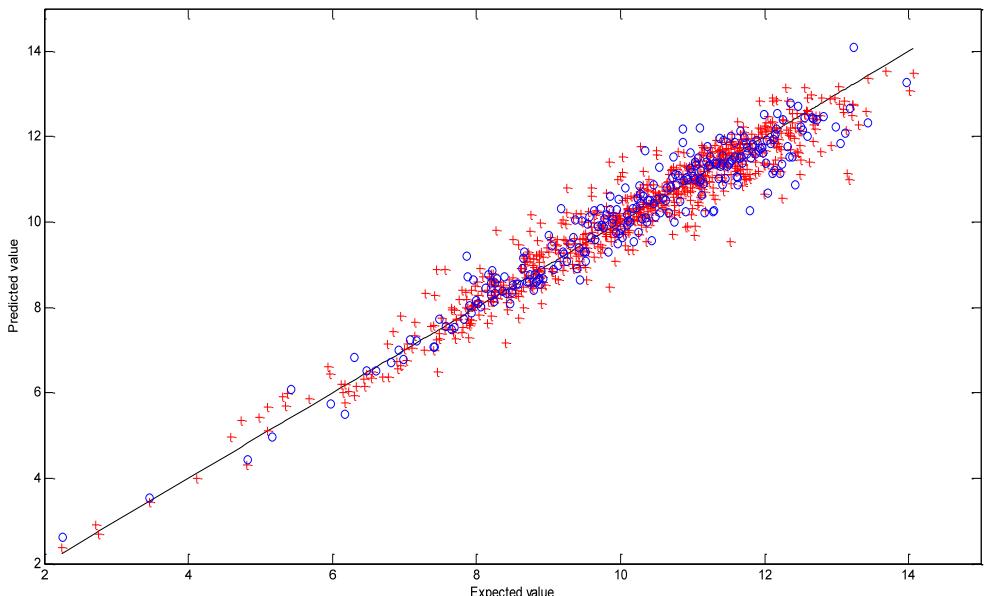
Root mean square error of prediction, RMSEP

$$RMSEP = \sqrt{\sum_{i=1}^m \frac{(y_i - \hat{y}_i)^2}{m}}$$

Average Ratiive Predictive Error, ARPE

$$ARPE = \sum_{i=1}^m \frac{|y_i - \hat{y}_i|}{m} \times 100\%$$

Model for Tar



'+' : Calibration samples, 'o': Test samples

Calibration Sample: 724

Test Sample: 241

Variable: 19

$RMSEP_{cal}=0.47$

$ARPE_{cal}=3.5\%$

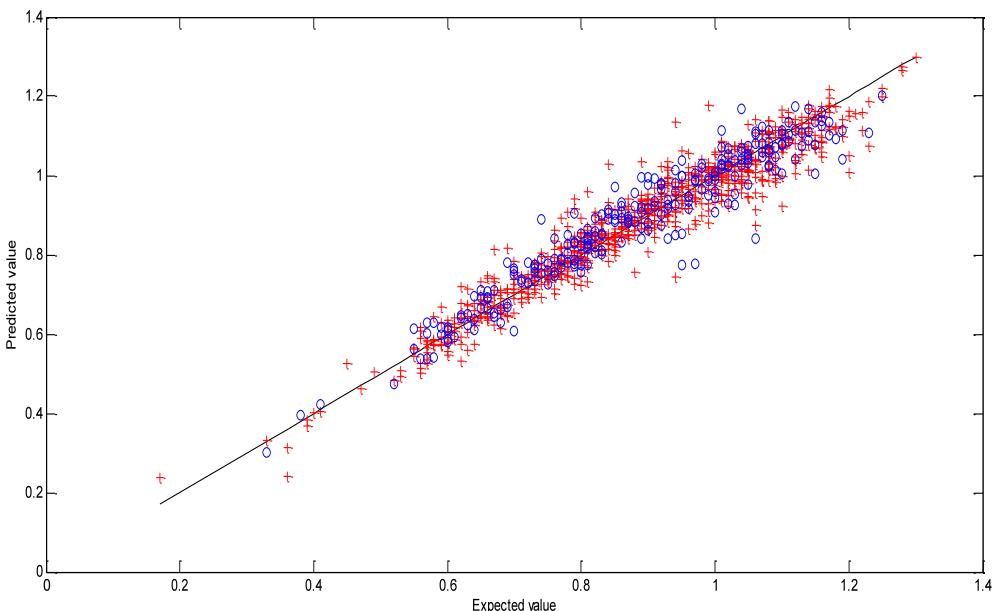
$R^2_{cal}=0.93$

$RMSEP_{test}=0.48$

$ARPE_{test}=3.6\%$

$R^2_{test}=0.93$

Model for Nicotine



'+' Calibration samples, 'o': Test samples

Calibration Sample: 744

Test Sample: 248

Variable: 19

$RMSEP_{cal}=0.05$

$ARPE_{cal}=4.2\%$

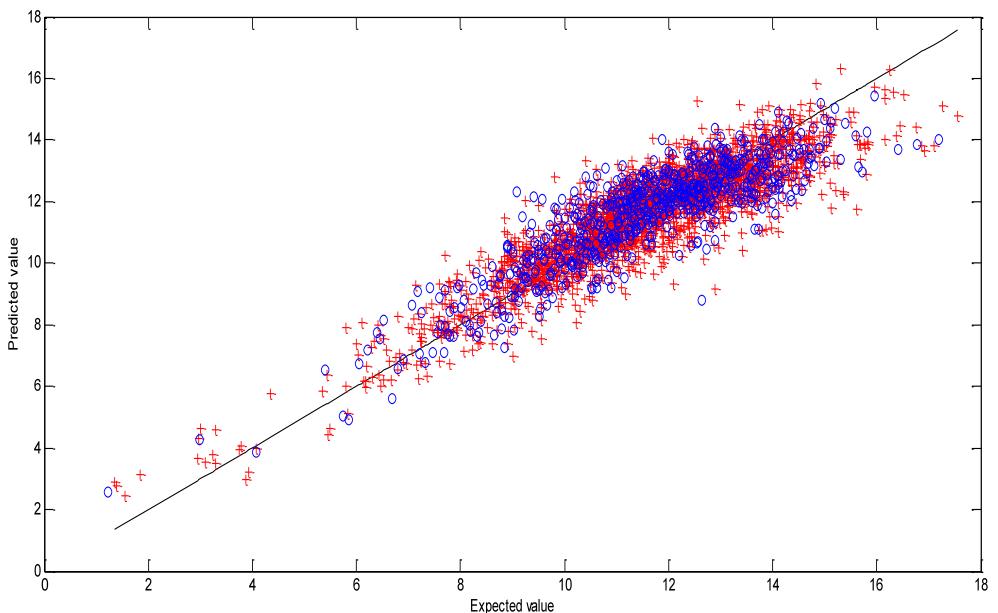
$R^2_{cal}=0.93$

$RMSEP_{test}=0.05$

$ARPE_{test}=4.5\%$

$R^2_{test}=0.91$

Model for CO



'+' : Calibration samples, 'o' : Test samples

Calibration Sample: 2110

Test Sample: 697

Variable: 20

$RMSEP_{cal}=0.91$

$ARPE_{cal}=6.5\%$

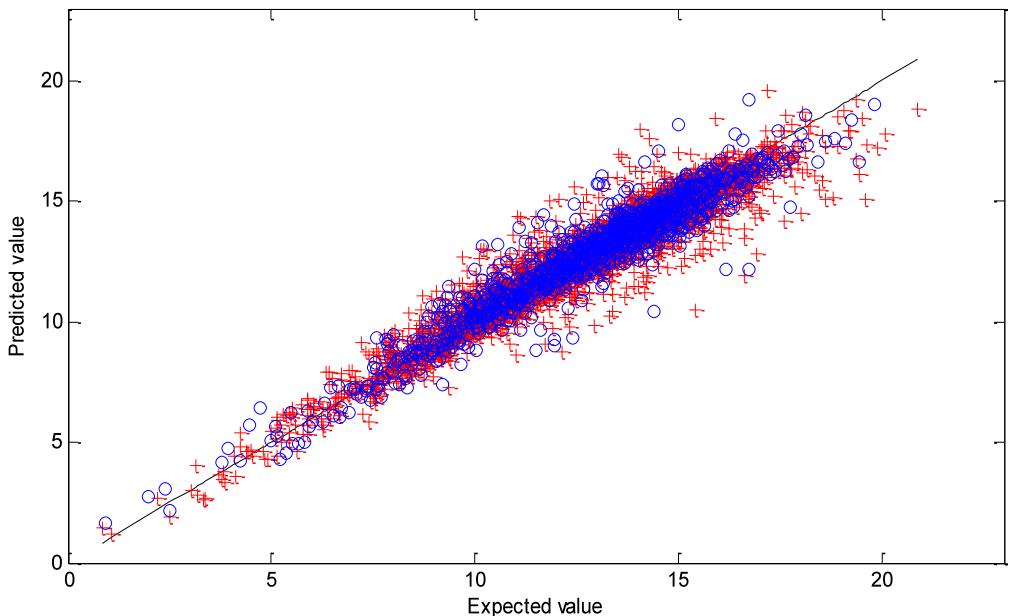
$R^2_{cal}=0.80$

$RMSEP_{test}=0.96$

$ARPE_{test}=6.8\%$

$R^2_{test}=0.77$

Model for TPM



'+' : Calibration samples, 'o' : Test samples

Calibration Sample: 3420

Test Sample: 1147

Variable: 22

$\text{RMSEP}_{\text{cal}} = 0.75$

$\text{ARPE}_{\text{cal}} = 4.3\%$

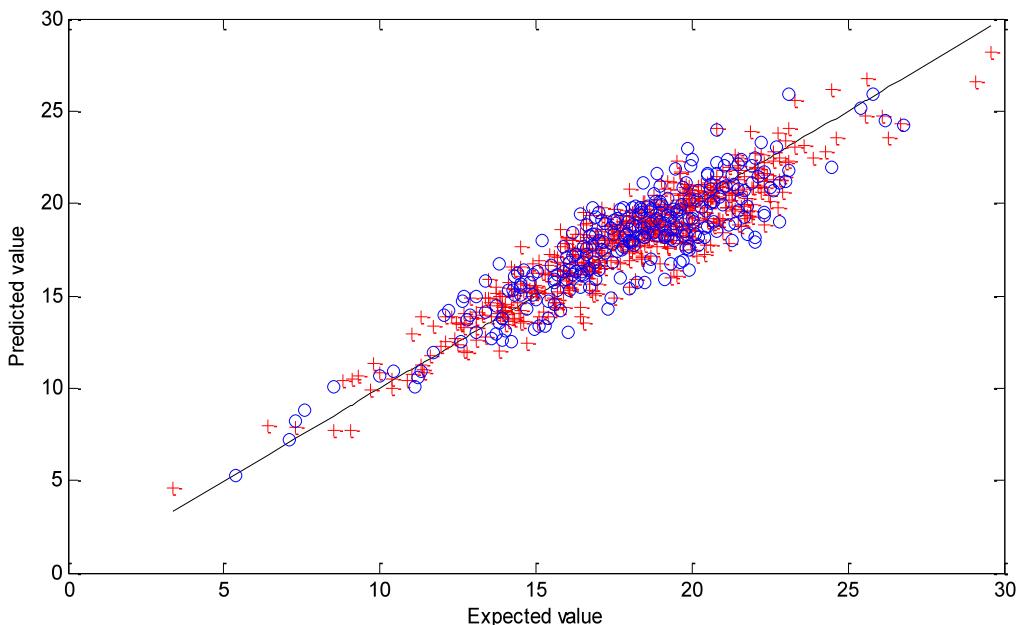
$R^2_{\text{cal}} = 0.92$

$\text{RMSEP}_{\text{test}} = 0.77$

$\text{ARPE}_{\text{test}} = 4.6\%$

$R^2_{\text{test}} = 0.91$

Model for Crotonaldehyde



'+' : Calibration samples, 'o': Test samples

Calibration Sample: 527

Test Sample: 262

Variable: 19

$\text{RMSEP}_{\text{cal}} = 1.25$

$\text{ARPE}_{\text{cal}} = 5.7\%$

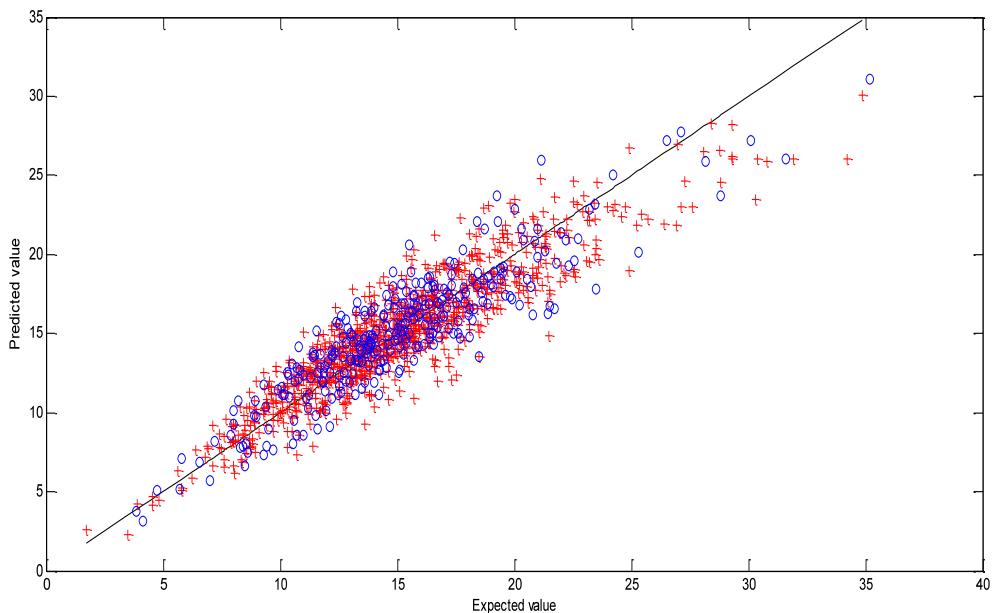
$R^2_{\text{cal}} = 0.86$

$\text{RMSEP}_{\text{test}} = 1.52$

$\text{ARPE}_{\text{test}} = 6.8\%$

$R^2_{\text{test}} = 0.79$

Model for PhOH



'+' : Calibration samples, 'o' : Test samples

Calibration Sample: 897

Test Sample: 292

Variable: 20

$\text{RMSEP}_{\text{cal}} = 1.81$

$\text{ARPE}_{\text{cal}} = 9.5\%$

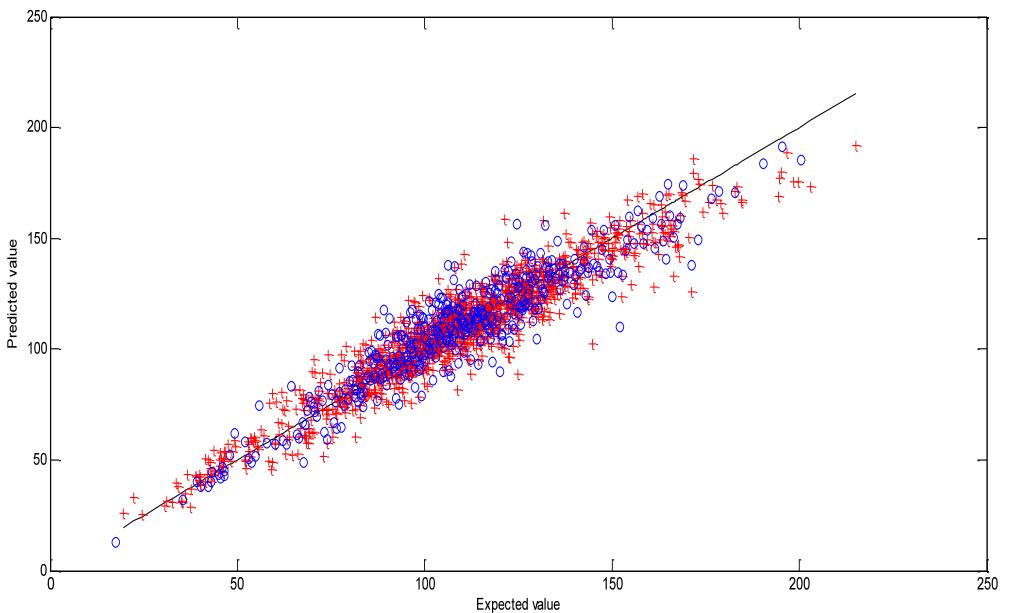
$R^2_{\text{cal}} = 0.83$

$\text{RMSEP}_{\text{test}} = 1.93$

$\text{ARPE}_{\text{test}} = 10.5\%$

$R^2_{\text{test}} = 0.81$

Model for HCN



'+' : Calibration samples, 'o' : Test samples

Calibration Sample: 1237

Test Sample: 409

Variable: 23

$RMSEP_{cal}=9.3$

$ARPE_{cal}=6.8\%$

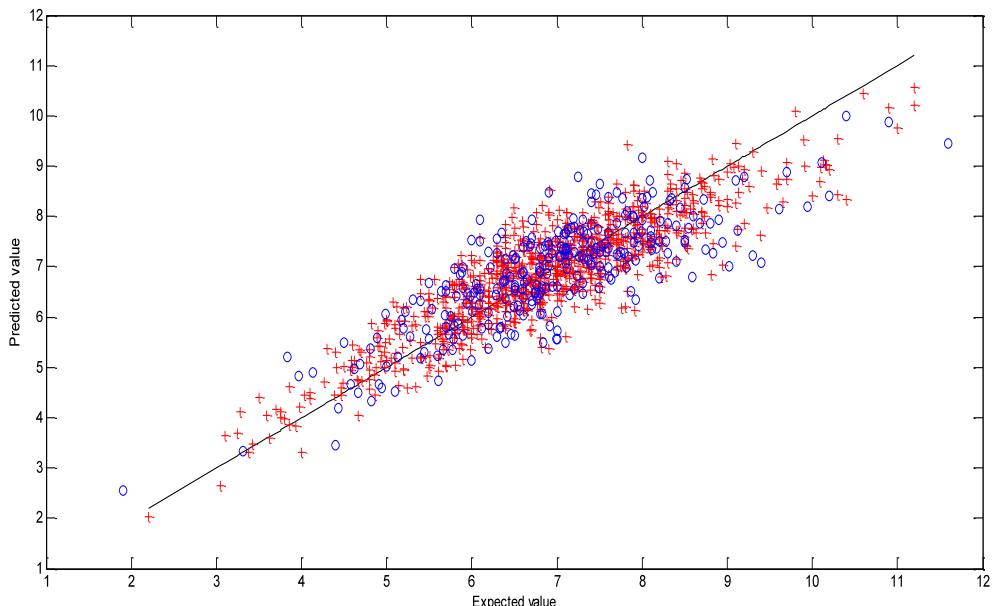
$R^2_{cal}=0.90$

$RMSEP_{test}=10.5$

$ARPE_{test}=7.5\%$

$R^2_{test}=0.86$

Model for NH₃



'+' : Calibration samples, 'o': Test samples

Calibration Sample: 896

Test Sample: 286

Variable: 23

RMSEP_{cal}=0.60

ARPE_{cal}=7.0%

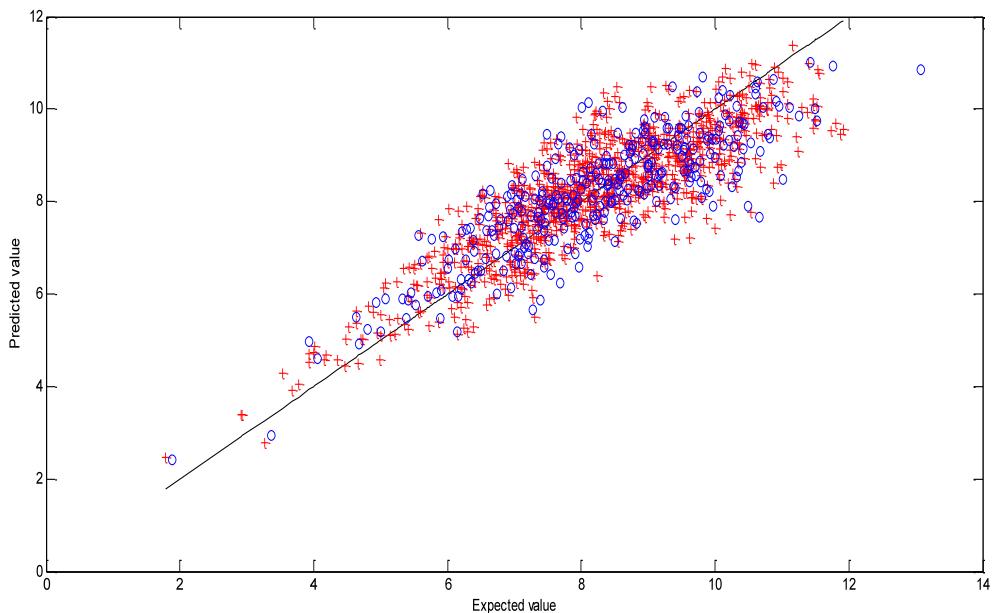
R²_{cal}=0.78

RMSEP_{test}=0.74

ARPE_{test}=8.5%

R²_{test}=0.66

Model for B[a]P



'+' : Calibration samples, 'o': Test samples

Calibration Sample: 964

Test Sample: 322

Variable: 21

$RMSEP_{cal}=0.82$

$ARPE_{cal}=8.2\%$

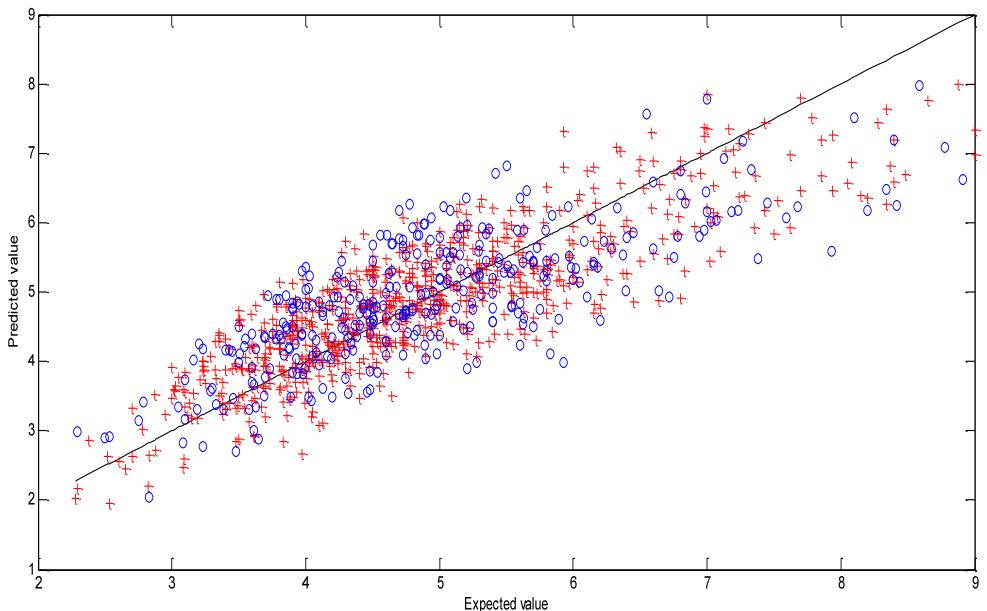
$R^2_{cal}=0.72$

$RMSEP_{test}=0.86$

$ARPE_{test}=8.5\%$

$R^2_{test}=0.70$

Model for NNK



'+' : Calibration samples, 'o' : Test samples

Calibration Sample: 708

Test Sample: 330

Variable: 12

$RMSEP_{cal}=0.64$

$ARPE_{cal}=10.6\%$

$R^2_{cal}=0.71$

$RMSEP_{test}=0.76$

$ARPE_{test}=12.4\%$

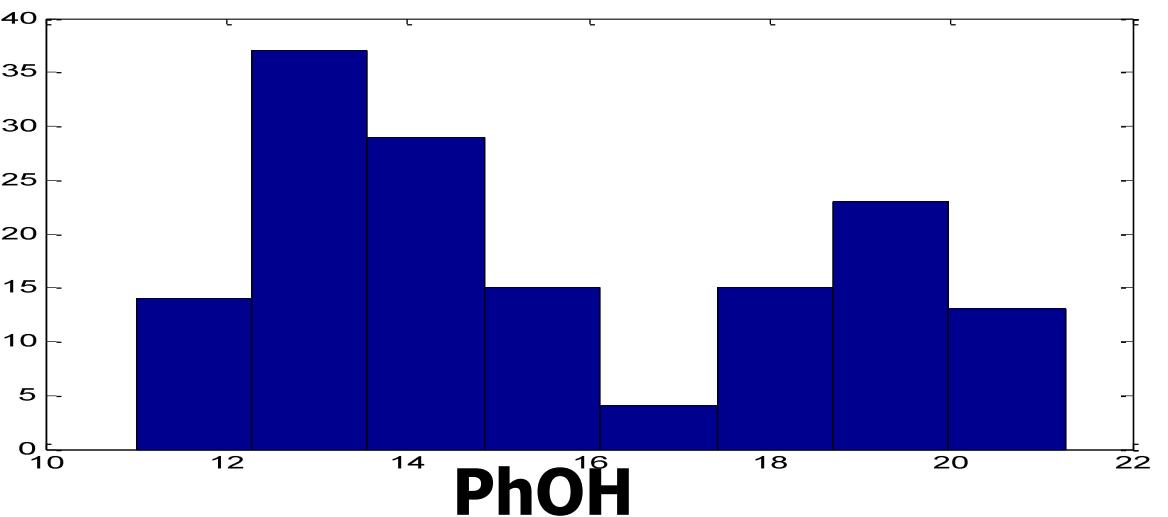
$R^2_{test}=0.59$

ARPE of the models

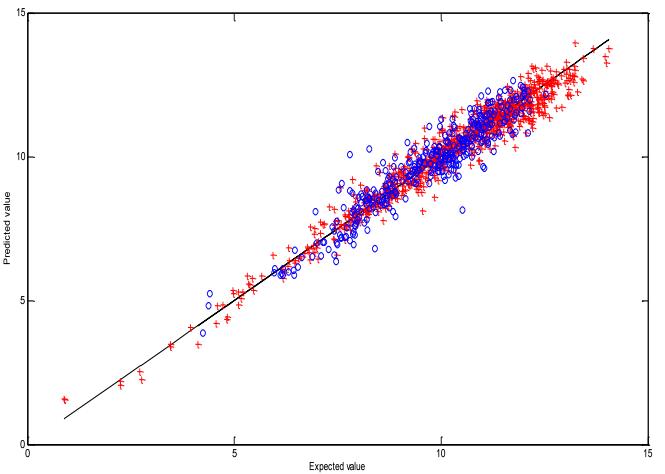
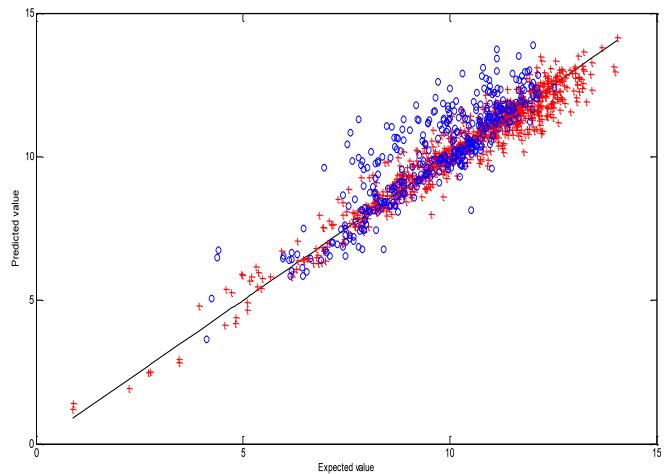
Milligram Components			Microgramme Components			Nanogram Components		
Tar	3.1%	~5%	Crot.	6.8%	~10%	B[a]P	8.5%	<15%
Nic	4.5%	~5%	PhOH	10.5%	~10%	NNK	12.4%	<15%
CO	6.8%	~5%	HCN	7.5%	~10%			
TPM	3.0%	~5%	NH3	8.5%	~10%			

Cigarette variability

	Tar	Nic	CO	HCN	NNK	NH3	BaP	PhOH	Crot
Mean	9.13	0.84	9.75	88.75	3.81	7.21	9.90	15.61	18.60
SD	0.51	0.04	0.42	10.15	0.33	0.49	0.61	2.95	1.05
CV	5.54	4.53	4.32	11.44	8.55	6.78	6.13	18.91	5.66



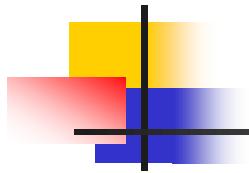
Model updating



Tar Model

Prediction errors of model updating

	ARPE1	ARPE2	Updating Samples		ARPE1	ARPE2	Updating Samples
Tar	7.5%	4.4%	39	Crot.	8.3%	8.2%	23
Nic	6.5%	5.6%	39	PhOH	10.9%	10.3%	43
CO	7.9%	6.6%	42	NNK	14.2%	14.1%	36
HCN	13.2%	11.2%	43	B[a]P	9.1%	7.8%	41
NH3	9.5%	8.3%	41				



Conclusions

- Prediction models are established for yields of several smoke components by using FT-NIRs of smoke particulate matter. This method works rapidly, accurately and can detect multiple components simultaneously.
- The proposed method can be extended to other smoke components by supplementing new models, the efficiency of the proposed method is improved with the increase of the number of established models.
- The proposed method is particularly applicable to the evaluation and control on variability of cigarette manufacturing.

*Thank you for
your attention!*