



Smoke Analytes Sub-Group (SMA) Report 2018

CORESTA Congress

“Science and Innovation: Addressing the Needs”

Kunming, October 25, 2018



SMA SG Objectives

- ❖ **To propose and maintain CORESTA Recommended Methods (CRMs) and related documents for the analysis of smoke constituents from combustible tobacco products.**
- ❖ **To organise interlaboratory testing related to Objective 1.**



SMA SG at a glance

❖ SG Coordinator

- Jana Jeffery, British American Tobacco Ltd, UK

❖ SG Secretary

- Rana Tayyarah, ITG Brands LLC, USA

❖ SC Liaison

- Martin Blumenstock, British American Tobacco Ltd, Germany

❖ SG members and meetings

- Generally 30-40 participants
- Usually two meetings per calendar year
- Last meeting Guildford, UK on 16th April 2018 (35 delegates)
- Next meeting Richmond, Virginia, USA on 9th April 2019



Areas of work 2018

Area	Activity
Documents	<ul style="list-style-type: none">• Technical reports• Periodic CRM review• CRM promotion to ISO standards
Cigarettes	<ul style="list-style-type: none">• Aromatic amines in mainstream smoke by GC/MS (project 48)• Next analytes of interest
Cigars	<ul style="list-style-type: none">• Strategy for cigar methods
Proficiency testing	<ul style="list-style-type: none">• Review opportunities for PT

Area	Activity	Status
Technical reports	<ul style="list-style-type: none"> • 2015 CS - Ammonia by IC • 2014 CS – Phenols by HPLC-FLD • 2017 CS - Aromatic Amines by GC/MS • 2017 Joint Experiment – Aromatic Amines by LC-MS/MS 	<ul style="list-style-type: none"> • Completed • In progress* • Submitted • Started*
Periodic CRMs review	<ul style="list-style-type: none"> • CRM 58 – B[a]P by GC/MS • CRM 70 – VOCs by GC/MS • CRM 74 – Carbonyls by HPLC/UV 	<ul style="list-style-type: none"> • Completed
	<ul style="list-style-type: none"> • CRM 78 - Phenols by HPLC-FLD • CRM 63 –TSNAs by GC/TEA 	<ul style="list-style-type: none"> • Board review* • In progress*

CS= Collaborative Study

**target completion end 2018*



ISO Standardisation Methods in progress

Standard	Activity	Status
ISO 22634-1/2 B[a]P in MS (WG 14)	Technical comments during FDIS	NWIP for a standard revision
ISO/FDIS 21160 Carbonyls in MS* (based on CRM 74)	Both approved as ISO/FDIS	Standards under publication
ISO/FDIS 2133 VOCs in MS* (based on CRM 70)		

MS = mainstream cigarette smoke



ISO Standardisation

Next candidate methods

- ❖ **Determination of ammonia in mainstream cigarette smoke by Ion Chromatography (2018)**
- ❖ **Determination of selected phenolic compounds in mainstream cigarette smoke by HPLC-FLD (2019)**



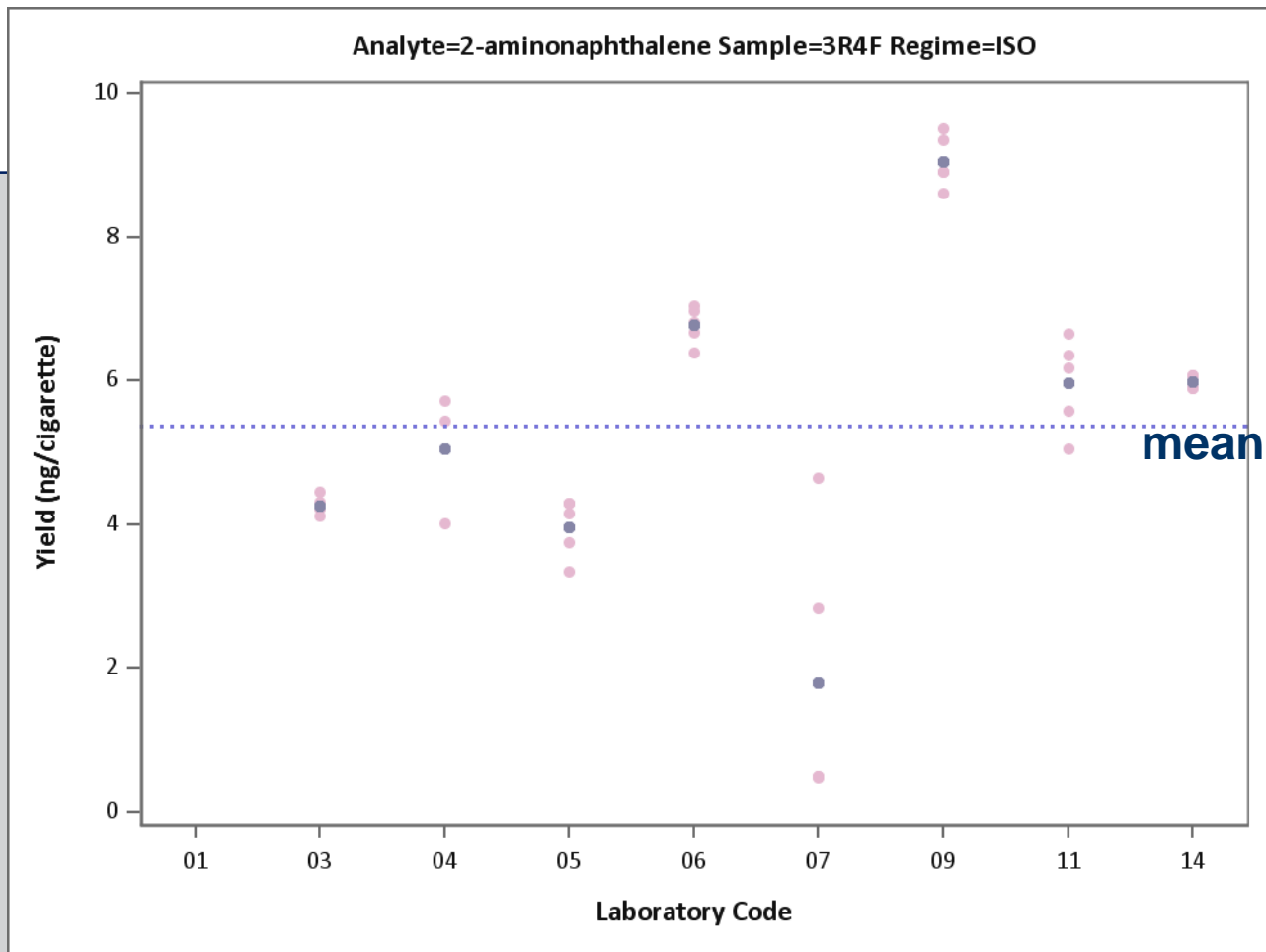
Aromatic amines by GC/MS (Project 48)

❖ Activities conducted in 2017-2018

- **Target analytes:** o-Toluidine, 2,6-Dimethylaniline, o-Anisidine, 1-Aminonaphthalene, 2-Aminonaphthalene, 3-Aminobiphenyl, 4-Aminobiphenyl
- **CS conducted (2017)**
 - 11 laboratories
 - 7 samples (4 commercial products, 3 reference products)
 - Smoking regime: ISO and Health Canada Intense (HCI)
- **Results - r&R high and varied. Repeatability ranged between 15-64% of the mean and reproducibility between 32-193% of the mean.**



- ❖ 2-aminonaphthalene
- ❖ 3R4F
- ❖ ISO smoking regime





Aromatic amines by GC/MS (Project 48)

- ❖ **Small focus group (5 laboratories) conducted a series the experiments to assess critical parameters of the method and develop a qualifier test**
 - **Internal standards**
 - **Solvents for standards**
 - **Matrix effects and recoveries**
 - **Solid Phase Extraction (SPE) clean-up conditions**

- ❖ **Method revision**



Aromatic amines by GC/MS

Kunming meeting

❖ Options discussed

- Test the method on a small scale CS using reference products
- Issue the CRM with the data from the existing CSs results with reasons for high r and R
- Close the project



Aromatic amines by GC/MS

Next steps

❖ Small scale CS

- Maximum 8 laboratories
- Three products: 1R6F, 1R5F, CM8
- Study provided qualifier sample
- Smoking regimes: ISO and CI regimes
- Five replicates per product per smoking regime

❖ Results for review for spring 2019 SMA meeting

❖ Technical report, guidance document

❖ Next analytes for CRM development

➤ Priority list from two surveys

- HCN, NO_x, semi-volatiles

❖ Comparison of TobLabNet methods and CRMs (review)

Analytes	CRM	TobLabNet method	Status
TSNAs	75	SOP 3	Completed
B[a]P	58	SOP 5	In progress
Aldehydes	74	SOP 8	Not started
VOCs	70	SOP 9	Not started

❖ Proficiency Testing

- Collaboration with University of Kentucky to extend existing PT scope
 - HCN and NOx as a pilot

❖ Current activities

- **NWIP 174 for testing CRMs for B[a]P and TSNAs on emissions from machine made cigars**



Future studies

- ❖ Documents
- ❖ Cigarettes
- ❖ Proficiency testing
- ❖ Cigars



Documents Outlook 2019

Area	Activity	Next step
Technical reports	<ul style="list-style-type: none">Aromatic Amines by GC/MS (project 48) focus group	<ul style="list-style-type: none">Complete small scale CS
Periodic CRMs review	<ul style="list-style-type: none">CRM 83 – Ammonia by IC	<ul style="list-style-type: none">NWIP
CRMs to ISO	<ul style="list-style-type: none">CRM 83 – Ammonia by ICCRM 78 - Phenols by HPLC-FLD	<ul style="list-style-type: none">NWIP
Methods comparison	<ul style="list-style-type: none">TobLabNet SOP 8 vs CRM 74TobLabNet SOP 9 vs CRM 70	<ul style="list-style-type: none">NWIPNWIP



❖ Cigarettes

- **Methods survey and data mining for HCN, NO_x and semi-volatiles. Timeline: spring 2019 meeting**
- **Aromatic amines by GC/MS (project 48)**



❖ Proficiency testing

- In collaboration with UofK conduct PT trial on HCN and NOx
- Set up PT calendar – analytes, products, frequency

❖ Smoke methods for cigars

- Scope extension of cigarette CRMs (B[a]P, TSNAs) to machine made cigars (NWIP 174)
- Combined methods (B[a]P, TSNAs, VOCs)

Area	Item	Plan
Cigarettes	Project 48 - AA GC/MS small scale CS	Spring 2019 meeting
	Method survey, data mining HCN, NOx, semi-volatiles	Spring 2019 meeting
PT	HCN, NOx pilot study	Spring 2019
Cigars	Scope extension of CRMs for B[a]P and TSNAs Combined methods (B[a]P, TSNAs, VOCs)	Q4 19 2020
Documents	Project 48 – supporting documents	As per schedule
	TR phenols in MS (project 162)	Complete by Q4 18
	2019 CRM review	Complete by Q2 19
	ISO promotions – ammonia, phenols	NWIP in Q4 18/Q1 19
	TobLabNet methods vs CRMs review	2019



Acknowledgements

- ❖ To all laboratories participating in SMA projects
- ❖ To all participants on SMA meeting, their contributions and engagement

Thank you for your attention





Project 48: Aromatic Amines by GC/MS

Methods summary

Parameter	Original method	Proposed method
Smoking	MS smoke collected on CFP	
ISTD addition on CFP	2,6-Dimethylaniline-d11 2-Aminonaphthalene-d7 4-Aminobiphenyl-d9 o-Toluidine-d9	2,6-Dimethylaniline-d11 2-Aminonaphthalene-d7 4-Aminobiphenyl-d9 o-Toluidine-d9 2-Methoxy-d3-aniline (o-Anisidine d3) 1-Aminonaphthalene-d7 3-Aminobiphenyl-d9
Solvent for standards	Ethyl acetate/n-hexane	Dichloromethane (DCM)
Extraction	dichloromethane (DCM), shaker	
Derivatisation	heptafluorobutyric anhydride (HFBA) , 40 minutes	
SPE clean up	Florisil (3g/12mL), elution in DCM	Florisil (2g/6 or 12mL), elution in DCM
Analysis	GC/MS-NCI (SIM)	

➤ **Target analytes:** o-Toluidine, 2,6-Dimethylaniline, o-Anisidine, 1-Aminonaphthalene, 2-Aminonaphthalene, 3-Aminobiphenyl, 4-Aminobiphenyl

Project 48: Aromatic Amines by GC/MS

CS r and R data

1-aminonaphthalene

Sample	Regime	N	Mean (ng/cigarette)	Repeatability		Reproducibility	
				r (ng/cigarette)	r (%)	R (ng/cigarette)	R (%)
1R6F	HCI	8	21,9	5,0	22,7	11,8	53,9
	ISO	8	12,4	2,8	22,6	4,1	32,9
3R4F	HCI	9	22,6	6,3	27,9	15,8	70,1
	ISO	9	11,0	2,2	20,0	6,6	59,4
CM8	HCI	10	32,5	12,5	38,5	28,1	86,5
	ISO	10	15,9	3,4	21,3	15,3	95,8

2-aminonaphthalene

Sample	Regime	N	Mean (ng/cigarette)	Repeatability		Reproducibility	
				r (ng/cigarette)	r (%)	R (ng/cigarette)	R (%)
1R6F	HCI	10	12,0	2,9	23,8	10,5	87,7
	ISO	9	6,6	1,8	27,4	4,8	73,3
3R4F	HCI	11	13,2	3,4	25,6	10,5	78,9
	ISO	9	6,2	1,8	29,1	4,6	74,9
CM8	HCI	10	15,9	4,4	27,8	14,0	88,0
	ISO	10	8,1	2,1	25,8	6,0	74,0

Abbreviations: N - number of data sets, r - repeatability, R - reproducibility



Project 48: Aromatic Amines by GC/MS

CS r and R data

3-aminobiphenyl

Sample	Regime	N	Mean (ng/cigarette)	Repeatability		Reproducibility	
				r (ng/cigarette)	r (%)	R (ng/cigarette)	R (%)
1R6F	HCI	11	3,5	1,1	30,0	3,9	109,7
	ISO	10	1,6	0,4	25,2	1,8	114,9
3R4F	HCI	11	4,0	1,2	29,6	4,5	112,2
	ISO	10	1,7	0,5	26,8	1,5	91,0
CM8	HCI	10	4,0	1,0	23,8	4,7	117,3
	ISO	11	1,9	0,5	26,1	2,3	121,2

4-aminobiphenyl

Sample	Regime	N	Mean (ng/cigarette)	Repeatability		Reproducibility	
				r (ng/cigarette)	r (%)	R (ng/cigarette)	R (%)
1R6F	HCI	10	2,4	0,6	26,2	2,8	116,4
	ISO	10	1,0	0,3	30,5	1,2	111,9
3R4F	HCI	11	2,8	0,7	25,9	3,0	106,4
	ISO	10	1,1	0,7	64,4	1,4	130,4
CM8	HCI	11	2,5	0,8	30,3	2,8	112,6
	ISO	11	1,2	0,3	26,2	1,3	111,8

Abbreviations: N -number of data sets, r -repeatability, R - reproducibility



Project 48: Aromatic Amines by GC/MS

CS r and R data

O-toluidine

Sample	Regime	N	Mean (ng/cigarette)	Repeatability		Reproducibility	
				r (ng/cigarette)	r (%)	R (ng/cigarette)	R (%)
1R6F	HCI	9	67,7	17,4	25,7	53,4	78,9
	ISO	7	36,7	7,8	21,3	12,2	33,2
3R4F	HCI	8	79,5	15,7	19,8	42,1	52,9
	ISO	9	34,8	7,4	21,2	24,4	70,0
CM8	HCI	9	94,3	30,6	32,5	75,2	79,8
	ISO	8	54,1	11,4	21,1	29,6	54,7

O-anisidine

Sample	Regime	N	Mean (ng/cigarette)	Repeatability		Reproducibility	
				r (ng/cigarette)	r (%)	R (cigarette)	R (%)
1R6F	HCI	9	2,9	1,3	45,4	3,5	121,4
	ISO	8	1,6	0,6	36,3	1,8	116,5
3R4F	HCI	9	3,1	0,9	30,1	3,0	97,8
	ISO	8	1,5	0,4	26,2	1,6	101,3
CM8	HCI	9	5,3	2,1	39,3	5,7	106,2
	ISO	9	2,9	0,7	24,7	3,4	117,6

Abbreviations: N - number of data sets, r - repeatability, R - reproducibility



Project 48: Aromatic Amines by GC/MS

CS r and R data

Sample	Regime	N	Mean (ng/cigarette)	Repeatability		Reproducibility	
				r (ng/cigarette)	r (%)	R (ng/cigarette)	R (%)
1R6F	HCI	8	8,3	4,0	48,1	11,0	131,5
	ISO	6	3,8	1,4	35,7	1,7	44,8
3R4F	HCI	8	9,1	4,6	50,9	14,5	159,7
	ISO	6	2,8	1,2	44,1	1,8	62,9
CM8	HCI	8	13,0	4,7	36,3	12,0	92,2
	ISO	7	6,9	1,7	24,5	4,9	71,5

Abbreviations: N -number of data sets, r -repeatability, R - reproducibility