Determination of Selected Volatiles in Cigarette Mainstream Smoke. The CORESTA 2008 Joint Experiment*

by

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SUMMARY

Joint experimental work carried out in 2006 by the CORESTA Special Analytes Task Force compared yield data on a wide range of smoke constituents obtained from reference cigarettes according to the existing methods used by participants. This work identified that the methodologies that were used to determine yields of selected volatiles in mainstream smoke under the ISO smoking regime would benefit from further joint experiments.

This report describes the output from the 2008 Joint Experiment on selected volatiles in smoke (1,3-butadiene, benzene, toluene, acrylonitrile, and isoprene). Its objectives were to investigate the main weaknesses and influencing factors in methodologies used by the participating laboratories and their effects on yield variability before deciding on one to take forward to a CORESTA recommended method. The Task Force considered this step was necessary before progressing to a full collaborative study using a recommended method. An experimental protocol was devised to investigate several factors such as the use of different calibration standards and the efficiencies of different trapping systems. The effects of other general factors identified from supplied methodology information as differing across laboratories were also analysed. A statistical assessment was made of their possible influence on smoke yields and yield reproducibility across different laboratories and is discussed in this report.

Between-laboratory variability has been reduced since the last study indicating that some laboratories have improved their methodology although extremely high values for the among-laboratory variability were still found for acrylonitrile (> 100%) and 1,3-butadiene (~ 80%) when related to the mean yields.

The means to reduce the variability in acrylonitrile and 1,3-butadiene yields are not apparent from the data and interpretations made in this study. However, when the different laboratories use the same methodology during the development of a recommended method at the next development stage then it is hoped that this high level of variability for acrylonitrile and 1,3-butadiene will be reduced to similar levels to those found for benzene, toluene, and isoprene.

As in previous work, it was recognised that although a more intense smoking regime may be introduced into the regulatory arena in the future, it was decided that the current ISO smoking regime should be used for this joint experiment.

A wider range of product styles will be investigated when the Task Force works towards a recommended method to take account of differing blends and designs and the potentially greater product variability of commercial products. This will provide robust estimates of within-laboratory repeatability and among-laboratory reproducibility and is intended to be reported in a later paper. [Beitr. Tabakforsch. Int. 24 (2011) 174–186]

ZUSAMMENFASSUNG

Zur quantitativen Bestimmung von flüchtigen organischen Verbindungen wie 1,3-Butadien, Isopren, Acrylonitril, Benzol und Toluol in der Gasphase des Hauptstromrauchs von Zigaretten wurde von der CORESTA eine Methode entwickelt, standardisiert und kürzlich veröffentlicht. Die Gasphase des Hauptstromrauchs wird dabei in gekühlten Flüssigfallen gesammelt und anschließend mittels Gaschromatographie und Massenspektrometrie getrennt und quantifiziert.

In der vorliegenden Arbeit werden die Ergebnisse der finalen Studie mit der standardisierten Methode berichtet. Die zusätzlichen experimentellen Informationen zur Methode sollen dazu beitragen, Laboratorien, die diese Methode einführen, in die Lage zu versetzen, robuste und reproduzierbare Daten zu erzeugen.

Im Rahmen der Studie wurden Daten von 15 Industrie- und 4 unabhängigen Laboratorien übermittelt, wobei 6 lineare und 14 rotative Rauchmaschinen eingesetzt wurden.

Im Verlauf der Studie konnten die beteiligten Labore Lösungen zu verschiedenen methodischen Problemen erarbeiten und so insbesondere die zwischen den Laboren beobachteten Streuungen für 1,3-Butadien und Acrylonitril minimieren.

Gleichwohl sind die ermittelten Reproduzierbarkeiten wesentlich größer im Vergleich zu den Daten, die für Kondensat, Nikotin und Kohlenmonoxid in der entsprechenden ISO-Norm angegeben sind. Gibt man die Reproduzierbarkeiten (R) in Prozent der gemessenen Mittelwerte an, findet man für 1,3-Butadien 63–93%, für Isopren 36–62%, für Acrylonitril 41–101%, für Benzol 35–70% und für Toluol 27–116%. Produkte mit höheren Kondensatgehalten zeigten dabei die vergleichsweise geringeren Streuungen auf einem Niveau vergleichbar mit den in den CORESTA-Standardmethoden für B[a]P und tabakspezifische Nitrosamine veröffentlichten Daten. Produkte mit sehr niedrigen Kondensatgehalten wiesen sehr viel größere Streuungen auf. [Beitr. Tabakforsch. Int. 24 (2011) 174–186]

RESUME

En 2006, l'expérimentation conjointe réalisée par le groupe d'étude spécial d'analyse du CORESTA (Centre de Coopération pour les Recherches Scientifiques Relatives au Tabac) avait comparé des données de rendement provenant d'une large gamme de constituants de la fumée, obtenues à partir de cigarettes de référence. selon les méthodes existantes utilisées par les participants à l'essai. Ces travaux avaient mis en évidence que les méthodes habituellement utilisées pour déterminer les rendements des composants volatiles dans la fumée du courant principal, selon le régime de fumage de l'ISO, pourraient bénéficier d'expériences conjointes plus poussées.

Ce rapport décrit les résultats de l'expérience conjointe menée en 2008 portant sur une sélection de substances volatiles dans la fumée (1,3-butadiène, benzène, toluène, acrylonitrile et isoprène). Le but de cette expérience était d'étudier les principales faiblesses et les facteurs d'influence des méthodes utilisées par les laboratoires participants et leurs effets sur la variabilité des rendements, avant de sélectionner une méthode recommandée par le CORESTA. Le groupe d'étude a jugé cette étape nécessaire avant de passer à une étude pleinement collaborative utilisant une méthode recommandée. Un protocole expérimental a été conçu pour étudier différents facteurs tels que diverses normes de calibration et l'efficacité de différents systèmes de captage. Les effets d'autres facteurs généraux identifiés qui, selon les informations fournies relatives à la méthodologie, varient entre les laboratoires, ont également été analysés. Une évaluation statistique de leur influence potentielle sur les rendements de la fumée et sur la reproductivité des rendements entre les différents laboratoires est discutée dans ce rapport.

La variabilité inter-laboratoire a été réduite depuis la dernière étude, ce qui indique que certains laboratoires ont amélioré leur méthodologie bien que des chiffres très élevés de variabilité intra-laboratoires aient encore été constatés pour l'acrylonitrile (>100 %) et le 1,3-butadiène (environ 80 %) par rapport aux rendements moyens.

Les moyens de réduire la variabilité des rendements de l'acrylonitrile et du 1,3-butadiène ne sont pas évidents sur la base des données et des interprétations produites dans cette étude. Toutefois, lorsque différents laboratoires utiliseront la même méthodologie lors de l'élaboration d'une méthode recommandée au stade suivant de développement, on espère que ces taux élevés de variabilité de l'acrylonitrile et du 1,3-butadiène seront réduits à des niveaux similaires à ceux trouvés pour le benzène, le toluène et l'isoprène.

Tout comme lors de travaux précédents, il a été reconnu que bien qu'un régime plus intense puisse être introduit à l'avenir dans le cadre réglementaire, il a été décidé que le régime actuel de fumage de l'ISO devait être utilisé pour cette expérience conjointe.

Une gamme plus large de styles de produits sera étudiée lors du travail du groupe d'étude sur une méthode recommandée pour prendre en compte différents mélanges et conceptions et la plus grande variabilité potentielle de produits commerciaux. Cela fournira une estimation fiable des répétabilités intra-laboratoire et inter-laboratoire qui fera l'objet d'un futur rapport. [Beitr. Tabakforsch. Int. 24 (2011) 174–186]

PARTICIPATING LABORATORIES

A summary of the twenty participating laboratories and their principal investigators is given on the next page. The Task Force co-ordinators wish to acknowledge the excellent contributions of each principal investigator and their colleagues without which the work of the Task Force could not have been completed.

INTRODUCTION

A range of analytical methodologies has been reported for determining the cigarette mainstream smoke yields of selected volatile compounds identified as being of interest to public health authorities. These methodologies involve a variety of smoke collection and trapping systems such as those described in References 1–8.

Previous CORESTA joint experimental work (9) had compared data on a wide range of smoke constituents obtained from reference cigarettes according to the existing methods used by participants. It identified that the methodologies that were used to determine yields of selected volatiles in mainstream smoke under the ISO smoking regime would benefit from further work to investigate the main weaknesses and influencing factors in their yield variability before recommending a particular method. This paper describes that work.

Participating laboratories and institutions	Principal investigators
Altadis (France)**	Valerie Troude / Sandrine Destruhaut
Arista (USA)	Brad Norwood / Fraser Williamson
Arista Labs Europe (UK)	Tatiana Humphries / Helen Taylor
BAT – Souza Cruz (Brazil)	Waldenir Farias Braga
British American Tobacco (UK)	Jacqui Vella / Tina Mead
CNTC Beijing (China)	Jun Zhou
CNTC QSTC (China)	Hongwei Hou
CNTC ZhengZhou (China)**	Fuwei Xie
Chemisches und Veterinär-landesuntersuchungsamt Sigmaringen (Germany)	Jürgen Hahn
Filtrona International (UK) #	Joanne Walker
Imperial Tobacco Group / Reemtsma (Germany)	Michael Intorp / Steve Purkis
Japan Tobacco (Japan)	Takatsugu Hyodo
Japan Tobacco International (Austria)	Jutta Pani
KT&G (Korea)	Hyo-Keun Kim
Labstat (Canada)	Mehran Sharifi / Pete Joza
Lorillard (USA)	Rob Stevens
Philip Morris Research Laboratories (Germany)	Jörg Diekmann
Philip Morris International (Switzerland)	Michel Rotach
Philip Morris Sampoerna (Indonesia)	Bimo Haryo Progo / Rachmat Hidayat
Reynolds Tobacco (USA)	Bert Gordon / Linda Crumpler / William Coleman
Rothmans Benson and Hedges (Canada)	Jennifer DeGraaf / Ian Jenkins

** Laboratories provided two datasets from two different methodologies
# Laboratory provided methodology data but did not participate in the study

EXPERIMENTAL

Overview of the protocol and methodology

The selected volatiles, as discussed in this work, comprise 1,3-butadiene, isoprene, acrylonitrile, benzene, and toluene. As in other recent CORESTA Task Force work, each laboratory was requested to follow its own in-house methods analysing as many of the five analytes as was their normal practice.

The 2R4F Kentucky reference cigarette used in the previous study (9) has been superseded by the 3R4F although the former and latter give similar "nicotine-free dry particulate matter" (NFDPM) yields. The 3R4F and 1R5F reference cigarettes were used for testing, each sourced from a single batch isolated by the University of Kentucky. Five replicates were required for each analyte in three independent experiments, providing a total of 15 results for each analyte. Participants were asked to follow the smoking plans provided for rotary and linear machines. One of these replicates per smoking run was used to determine trapping efficiencies.

Five replicates were run over one or two consecutive days

and the two experiments were run with a minimum of one week or longer between each experiment; this was achieved by most laboratories.

The most important factors for study in this joint experiment were identified as the glass impinger trapping efficiency (from a series of one up to three impingers or as a combination of impingers and other trapping means) and the choice of calibration standard (both the use of the particular deuterated compound and the use of different sources of a particular deuterated compound). In addition, some laboratories volunteered to carry out vapour phase trapping into Tedlar bags although it was not decided by the Task Forceto develop a recommended method based on this methodology.

An overview of the details of selected volatiles methodology applied in each laboratory in 2008 is shown in Tables 1 and 2 to allow further investigation into whether any of the provided methodology parameters could be linked to yield variability. In some cases requested information was not provided by the laboratories.

RESULTS AND ANALYSIS

Variability of standard smoke parameters

Total Particulate Matter (TPM) and puff count data were received from all participating laboratories and are summarised in Table 3.

Laboratories smoked a range of cigarettes per replicate (2–20) for 1R5F and 3R4F. Eight laboratories used "linear" and 14 used "rotary" smoking machines for smoke collection giving very similar TPM and puff count data across both smoking machine types. As expected due to yield differences, the TPM yield variability for 3R4F was lower than for the 1R5F cigarette. The low puff count variability indicated good adherence to conditioning standards by the participating laboratories.

Statistical outliers / data removal

Seven extreme individual data points (< 0.2% of the full data-set) showing extremely non-homogenous distribution within data sets received from individual laboratories were identified by visual observation and were excluded from the subsequent statistical analysis shown in Table 4.

Smoke yields of 1,3-butadiene, toluene, benzene, acrylonitrile, and isoprene are given in Tables 5–9 respectively. Some laboratories seemed markedly higher or lower than most others for one or both samples, e.g. 1,3-butadiene (Laboratory 6), acrylonitrile (Laboratories 6, 10,12, 13, 15, and 19), and isoprene (Laboratory 18). These results were not removed because to do so would lead to artificially low estimates of among-laboratory variability that exists using the currently employed methods. However, these results perhaps suggest that there remains opportunity for reducing variability further during method standardisation, particularly for these analytes.

Some late data were received from laboratory 20 showing mean values for benzene and isoprene analysis but only for the 1R5F product. This was included in yield Tables 7 and 9 but not in the statistical analyses in Tables 10 and 11.

Table 1. Overview of smoking and trapping applied in selected volatiles methodologies.

Lab No.	Smoking machine	Cigs per replicate	CFP in set up	CFP extract incl. in yield	Trapping system	Impinger No.	Methanolic trapping solution (mL)	Impinger temp. (°C)	Dead vol. (mL)	Frit spec.	Glass beads in impinger	Tubing type
1	Rotary	20 and 20	yes	no	Tedlar	...	...	...	...	...	...	silicon
2	Rotary	20 and 20	yes	yes	impinger	2	50	−4 / −70	<10	none	no	tygon
3	Linear	5 and 5	yes	yes	impinger	3	60	< −70	5	coarse	no	tygon
4	Rotary	10 and 10	yes	yes	impinger	2	30	< −50	5	none	no	nalgene
5	Rotary	10 and 10	yes	no	impinger	2	40	< −70	<10	coarse	no	glass
6	Linear	10 and 10	yes	no	impinger	2	20	< −70	10	none	no	tygon / PVC
7	Rotary	10 and 10	yes	no	impinger	2	20	< −70	14	coarse	no	PE
8	Rotary	10 and 10	yes	yes	impinger	2	not provided	< −70	1.3	...	no	PVC
9	Linear	10 and 10	yes	no	impinger	3	20	< −70	5	fine	no	glass
10	Linear	5 and 5	yes	yes	impinger	3	20	< −70	<10	coarse	no	silicon
11	Linear	10 and 10	yes	no	impinger	3	not provided	< −70	2	none	no	glass
12	Rotary	10 and 20	yes	no	impinger	3	20	< −70	<3	none	yes	PVC
13	Rotary	10 and 20	yes	no	Tedlar	...	...	...	...	...	...	...
14	Rotary	10 and 10	yes	yes	impinger	3	60	< −70	10	coarse	no	PVC
15	Linear	2 and 2	yes	no	Tedlar	...	...	...	...	...	...	...
16	Linear	5 and 10	yes	yes	impinger	1	20	< −70	4.5	coarse	no	PVC
17	Rotary	10 and 10	yes	yes	impinger	3	not provided	< −70	2.5	coarse	no	latex
18	Rotary	5 and 5	yes	no	Tedlar	...	...	...	...	...	...	...
19	Rotary	20 and 20	yes	no	impinger	2	20	< −70	3–4	none	no	glass / polyurethane
20	Rotary	10 and ...	yes	no	impinger	2	20	< −70	8	none	no	silicon
21	Rotary	10 and 10	yes	yes	impinger	3	50	< −70	3–4	none	yes	tygon
22	Linear	10 and 10	yes	no	impinger + XAD	1 + XAD	not provided	< −70	1.1	none	no	silicon
23	Rotary	10 and 10	yes	no	impinger	2	100	< −70	2	none	no	PVC

Table 2. Overview of calibration applied in selected volatiles methodologies.

Lab No.	Calibration				Point of standard addition	No. of clearing puffs	Mass spectral quantifier / qualifier ions				
	with 'Restek' standard	Quadratic or linear	Through zero	For each volatile			1,3-Butadiene	Isoprene	Acrylonitrile	Toluene	Benzene
1	No	quadratic	yes	yes	after smoking / into Tedlar bag	0	53	67	26	...	78
2	Yes	linear	no	yes	into vial	6	...	...	...	...	...
3	Yes	linear	yes	yes	into impinger	5	53/54	67/68	53/52	91/92	77/78
4	No	linear	no	yes	into impinger	5	54/53	67/68	53/52,26	91/92	78/77
5	No	linear	yes	yes	into 2nd impinger	3	...	...	...	...	...
6	Yes	linear	yes	yes	into vial	6	...	...	...	...	...
7	No	linear	no	yes	into impinger	5	54/51,52	67/40,53	53/26,52	92/65,91	78/39,52
8	No	linear	yes	yes	into impinger	5	...	...	...	...	...
9	Yes	linear	no	yes	into impinger	methanol purge	...	...	...	...	...
10	Yes	linear	yes	yes	into impinger	5	54/53	67/68	52/53	91/92	78/77
11	No	linear	yes	yes	into vial	methanol purge	...	...	...	...	...
12	Yes	1/X	no	yes	into impinger	0	...	...	...	...	...
13	No	linear	no	yes	no standard	...	...	...	...	...	...
14	Yes	linear	no	yes	into impinger	2	54/53	67/68	53/52	91/92	78/77
15	No	linear	no	yes	no standard	2	...	...	...	...	...
16	Yes	linear	yes	yes	into impinger	1	54	67	52	91	78
17	Yes	linear	yes	yes	into impinger	3	54/53	67/68	52/53	91/92	78/77
18	No	linear	no	yes	into Tedlar bag	1	54/53,51	67/68,63	53/52,26	91/92,65	78/77,51
19	No	linear	no	no	into impinger	5	54/39,53,27	67/68,53,39	52/56,51,53	91/92, 65,39	78/77,51
20	No	linear	no	yes	into impinger	3	...	67	52	91	78
21	Yes	linear	yes	yes	into impinger	3	39/54,53	67/53,68	53/26,52	92/91	78/52,51
22	No	linear	yes	yes	into impinger	methanol purge	54/53	67/68	53/54	91/92	78/77
23	No	linear	no	yes	into impinger	2	54/53	67/68	53/54	91/92	78/77

Table 3. TPM (mg/cig) and puff count data measured on linear and rotary smoking machines.

Para-meter	Cigarette type	Overall		Linear		Rotary	
		Mean	CoV %	Mean	CoV %	Mean	CoV %
TPM	3R4F	10.6	7.5	10.9	5.5	10.5	7.6
	1R5F	2.4	16.7	2.6	15.4	2.4	12.5
Puff count	3R4F	8.3	3.6	8.4	4.8	8.4	2.3
	1R5F	6.9	4.3	6.9	5.8	6.9	2.9

Table 4. Removed data. Smoke yields of 1,3-butadiene, toluene, benzene acrylonitrile and isoprene are given in Tables 5–9 respectively.

Analyte	Sample	Lab No.	Run	Replicate	Yield
1,3-Butadiene	3R4F	8	3	2	47.9
	3R4F	12	1	4	10.5
Benzene	3R4F	6	2	1	48.3
Toluene	3R4F	18	1	1	49.0
Acrylonitrile	3R4F	12	1	4	21.0
	1R5F	13	2	2	3.17
Isoprene	3R4F	12	1	4	252

Comparison of mean values and variability with data from the last CORESTA study

A statistical analysis estimated within-laboratory and among laboratory variability values (named respectively as 'r' and 'R' in this work) among replicates and experiments found within the various participating laboratories. Although it used the same statistical equations, this approach did not estimate ISO defined repeatability and reproducibility because each laboratory did not follow a prescribed method protocol. Such an analysis is useful in identifying analytes that would most benefit from method standardisation. The statistical equations defining these 'r' and 'R' values obtained for both the 1R5F and 3R4F for each of the studied analytes are given in Table 10 and are based on those described in ISO 5725 (10). Such comparative methods were used in the previously described work (9, 11).

There was generally good agreement between the mean yields of the selected volatiles from 1R5F and 3R4F cigarettes obtained in the present study and those for 1R5F and 2R4F obtained in 2006 (Table 10).

Discrimination between 3R4F and 1R5F cigarettes

A method for the collection and analysis of selected volatiles will need to be fully standardised, if it is to be used for regulatory purposes. It was recognised within the Task Force that a study was required to assess currently available methods. Such a study would identify whether these analytes give similar results irrespective of the laboratory method used, whether certain aspects might be inherently flawed and which parts of the methodology need more detailed evaluation.

The assessment of both the method stability and the

Table 5. 1,3-Butadiene yields across laboratories.

Lab No.	Trapping system	'Restek' standard	Internal standard	Mean yield (μg/cig)	
				3R4F	1R5F
1	Tedlar	no	1,3-butadiene-d6	31.6	9.4
2	Impinger	yes	1,3-butadiene-d6	24.7	7.8
2	Impinger	no	benzene-d6	38.0	11.1
3	Impinger	yes	1,3-butadiene-d6	44.3	16.0
3	Impinger	no	benzene-d6	33.1	12.0
4	Impinger	yes	benzene-d6	35.1	10.0
5	Impinger	no	benzene-d6	37.1	11.3
6	Impinger	yes	1,3-butadiene-d6	15.4	9.8
6	Impinger	yes	benzene-d6	13.7	6.3
7	Impinger	no	toluene-d8	54.2	14.9
8	Impinger	no	acrylonitrile-d3	60.9	16.2
9	Impinger	yes	1,3-butadiene-d6	46.9	14.1
9	Impinger	no	benzene-d6	36.6	16.4
10	Impinger	yes	1,3-butadiene-d6	45.7	18.4
10	Impinger	no	benzene-d6	39.4	15.7
11	Impinger	no	benzene-d6	42.1	14.7
11	Impinger	no	toluene-d8	41.6	14.4
11	Impinger	no	acrylonitrile-d3	46.3	15.9
12	Impinger	yes	benzene-d6	31.3	10.1
13	Tedlar	no	external	66.4	20.7
14	Impinger	yes	1,3-butadiene-d6	42.2	13.1
14	Impinger	yes	benzene-d6	49.5	14.9
15	Tedlar	no	1,3-butadiene-d6	44.1	13.5
16	Impinger	no	1,3-butadiene-d6	42.5	12.3
16	Impinger	no	benzene-d6	30.1	7.7
17	Impinger	yes	1,3-butadiene-d6	29.7	10.0
17	Impinger	yes	benzene-d6	24.8	9.1
18	Tedlar	no	benzene-d6	24.1	7.7
19	Impinger	no	benzene-d6	38.4	12.1
21	Impinger	no	1,3-butadiene-d6	26.7	10.0
22	Imp.+ XAD	no	benzene-d6	42.5	13.7
22	Imp. + XAD	no	toluene-d8	42.8	13.5
22	Imp. + XAD	no	acrylonitrile-d3	46.3	15.4

Overall data - Mean yield in μg/cig (CoV%)

Overall data (33 data sets)	38.4 (30)	12.7 (27)
Data from Tedlar bag (4 data sets)	41.5 (45)	12.8 (45)
Data from impinger trapping (29 data sets)	38.0 (28)	12.6 (24)
Impinger data calibrated with 1,3-butadiene (10 data sets)	35.3 (30)	12.1 (27)
Impinger data calibrated with benzene (13 data sets)	35.1 (26)	11.9 (26)
Impinger data calibrated with toluene (3 data sets)	46.2 (15)	14.3 (5)
Impinger data calibrated with acrylonitrile (3 data sets)	51.1 (17)	15.8 (3)

expertise applied in the different laboratories used in this study is based on the similarity/dissimilarity of the data among laboratories. The statistical analysis of the effectiveness with which the array of laboratory methods used in the study for each analyte was able to differentiate between the 1R5F and 3R4F cigarettes is the means that was used to reach this objective. The statistical assessment is made on the basis that each of the two reference cigarettes would be

Table 6. Toluene yields across laboratories.

Lab No.	Trapping system	Internal standard	Mean toluene yield (µg/cig)	
			3R4F	1R5F
2	Impinger	toluene-d8	83.5	21.5
2	Impinger	benzene-d6	78.8	20.3
3	Impinger	toluene-d8	80.5	24.4
3	Impinger	benzene-d6	81.2	24.7
4	Impinger	benzene-d6	73.9	19.7
5	Impinger	benzene-d6	62.1	17.5
6	Impinger	toluene-d8	44.5	11.4
6	Impinger	benzene-d6	44.6	11.4
7	Impinger	toluene-d8	59.0	15.3
8	Impinger	toluene-d8	56.4	17.8
9	Impinger	toluene-d8	57.1	16.0
9	Impinger	benzene-d6	57.2	14.9
10	Impinger	benzene-d6	71.7	17.7
11	Impinger	benzene-d6	55.3	16.7
11	Impinger	toluene-d8	54.9	16.3
11	Impinger	acrylonitrile-d3	57.3	16.9
12	Impinger	toluene-d8	89.3	22.7
13	Tedlar	external	70.3	22.8
14	Impinger	toluene-d8	67.6	19.1
15	Tedlar	toluene-d8	57.8	16.4
16	Impinger	toluene-d8	73.5	16.0
16	Impinger	benzene-d6	76.5	16.6
17	Impinger	toluene-d8	35.5	9.2
17	Impinger	benzene-d6	39.1	9.9
18	Tedlar	benzene-d6	71.0	23.5
19	Impinger	benzene-d6	70.9	25.9
21	Impinger	toluene-d8	67.8	16.0
22	Impinger + XAD	benzene-d6	66.3	18.2
22	Impinger + XAD	toluene-d8	66.6	17.8
22	Impinger + XAD	acrylonitrile-d3	67.4	18.7

Overall data - Mean yield in µg/cig (CoV%)

Overall data (23 data sets)			64.6 (20)	17.8 (24)
Data from Tedlar bag (4 data sets)			66.3 (11)	20.9 (19)
Data from Impinger trapping (19 data sets)			64.4 (21)	17.5 (24)
Impinger data calibrated with benzene (14 data sets)			64.8 (21)	17.8 (26)
Impinger data calibrated with toluene (3 data sets)			64.3 (24)	17.2 (24)
Impinger data calibrated with acrylonitrile (2 data sets)			62.3 (12)	17.8 (7)
Data from labs including CFP in analysis (9 data sets)			68.2	18.0
Data from labs without CFP extraction in analysis (9 data sets)			63.6	18.0

Table 7. Benzene yields across laboratories.

Lab No.	Trapping system	Internal standard	Mean benzene yield (µg/cig)	
			3R4F	1R5F
1	Tedlar	benzene-d6	37.9	11.2
2	Impinger	benzene-d6	39.6	12.1
3	Impinger	benzene-d6	45.7	16.7
4	Impinger	benzene-d6	48.7	16.3
5	Impinger	benzene-d6	37.3	12.1
6	Impinger	benzene-d6	34.7	11.7
7	Impinger	toluene-d8	41.2	13.8
8	Impinger	benzene-d6	39.2	14.2
9	Impinger	benzene-d6	37.3	13.9
10	Impinger	benzene-d6	42.1	13.2
11	Impinger	benzene-d6	36.5	13.6
11	Impinger	toluene-d8	36.2	13.3
11	Impinger	acrylonitrile-d3	37.7	13.7
12	Impinger	benzene-d6	46.5	15.2
13	Tedlar	external	46.2	15.7
14	Impinger	benzene-d6	43.8	14.5
15	Tedlar	benzene-d6	38.4	11.2
16	Impinger	benzene-d6	43.5	12.1
17	Impinger	benzene-d6	24.8	7.7
18	Tedlar	benzene-d6	36.7	13.5
19	Impinger	benzene-d6	37.6	11.8
20	Impinger	benzene-d6	n.m. [a]	11.8
21	Impinger	benzene-d6	38.4	12.8
22	Impinger + XAD	benzene-d6	37.9	13.2
22	Impinger + XAD	toluene-d8	38.2	13.0
22	Impinger + XAD	acrylonitrile-d3	38.6	13.7

Overall data - Mean yield in µg/cig (CoV%)

Overall data (26 data sets)			39.4 (12)	13.2 (14)
Data from Tedlar bag (4 data sets)			39.8 (11)	12.9 (17)
Data from Impinger trapping (22 data sets)			39.3 (13)	13.2 (14)
Impinger data calibrated with benzene (17 data sets)			39.7 (15)	13.1 (16)
Impinger data calibrated with toluene (3 data sets)			38.5 (6)	13.4 (3)
Data from labs using frits (7 data sets, lab 17 excluded)			41.6	13.8
Data from labs without frits (12 data sets)			41.1	13.4
Data from labs using silicon tubing (6 data sets for 3R4F and 7 for 1R5F)			37.6	12.7

[a] not measured

tested by two different laboratories, together with the assumptions that each analyte is roughly correlated with NFDPM for these two reference cigarettes. Here, it is noted that on the NFDPM scale these two samples are distinctly different, with average yields of approximately 1.7 and 9.5 mg/cig, respectively.

This approach has been described in the last two reports from this Task Force (9, 11). The statistical equation is provided in Table 11 alongside the results of the statistical analysis. In summary, the data show that there has been some improvement for benzene and toluene but no improvement for 1,3-butadiene, acrylonitrile, and isoprene in differentiating between 1R5F and 3R4F since the 2006 study.

Effects of trapping efficiencies on smoke yields

All laboratories used methanol as their trapping solvent. Table 12 provides the trapping efficiencies in the various traps. Efficiency levels at 0% are equivalent to below the limit of quantification (< LOQ). The LOQs were not reported for this work. However, measured efficiencies may depend indirectly on the LOQs obtained by the

Table 8. Acrylonitrile yields across laboratories.

Lab No.	Trapping system	Internal standard	Mean acrylonitrile yield (µg/cig)	
			3R4F	1R5F
1	Tedlar	acrylonitrile-d3	8.9	2.8
2	Impinger	acrylonitrile-d3	7.2	1.8
2	Impinger	benzene-d6	6.9	1.8
3	Impinger	acrylonitrile-d3	8.0	2.3
3	Impinger	benzene-d6	8.2	2.3
4	Impinger	toluene-d8	10.9	2.3
5	Impinger	benzene-d6	7.8	1.9
6	Impinger	acrylonitrile-d3	18.8	14.2
6	Impinger	benzene-d6	19.3	14.3
7	Impinger	toluene-d8	8.1	2.0
8	Impinger	acrylonitrile-d3	7.8	2.0
9	Impinger	acrylonitrile-d3	8.5	2.0
9	Impinger	benzene-d6	8.0	1.6
10	Impinger	benzene-d6	11.5	6.1
11	Impinger	benzene-d6	7.8	2.2
11	Impinger	toluene-d8	7.8	2.2
11	Impinger	acrylonitrile-d3	8.1	2.3
12	Impinger	benzene-d6	24.4	7.2
13	Tedlar	external	17.3	4.1
14	Impinger	acrylonitrile-d3	7.0	1.8
15	Tedlar	acrylonitrile-d3	14.5	2.3
16	Impinger	acrylonitrile-d3	7.5	1.3
16	Impinger	benzene-d6	7.5	1.3
17	Impinger	acrylonitrile-d3	8.9	1.6
17	Impinger	benzene-d6	6.9	1.4
18	Tedlar	benzene-d6	7.4	2.0
19	Impinger	benzene-d6	22.2	1.9
21	Impinger	acrylonitrile-d3	6.6	3.1
22	Impinger + XAD	benzene-d6	7.8	2.2
22	Impinger + XAD	toluene-d8	7.9	2.2
22	Impinger + XAD	acrylonitrile-d3	8.0	2.3

Overall data - Mean yield in µg/cig (CoV%)

Overall data (31 data sets)	10.2 (48)	3.2 (101)
Data from Tedlar bag (4 data sets)	12.0 (39)	2.8 (33)
Data from impinger trapping (27 data sets)	10.0 (50)	3.2 (106)
Impinger data calibrated with benzene (12 data sets)	11.5 (56)	3.7 (105)
Impinger data calibrated with toluene (4 data sets)	8.7 (17)	2.2 (6)
Impinger data calibrated with acrylonitrile (12 data sets)	8.8 (37)	3.1 (113)

Table 9. Isoprene yields across laboratories.

Lab No.	Trapping system	Internal standard	Mean isoprene yield (µg/cig)	
			3R4F	1R5F
1	Tedlar	isoprene-d	272.1	91.3
2	Impinger	toluene-d8	352.5	114.0
2	Impinger	benzene-d6	333.2	107.8
3	Impinger	benzene-d6	340.8	129.2
3	Impinger	benzene-d6	340.9	129.3
4	Impinger	toluene-d8	338.0	100.8
5	Impinger	benzene-d6	318.0	103.9
6	Impinger	benzene-d6	344.9	108.5
7	Impinger	toluene-d8	411.4	129.3
8	Impinger	acrylonitrile-d3	301.7	99.9
9	Impinger	benzene-d6	403.4	155.8
10	Impinger	benzene-d6	374.4	130.2
11	Impinger	benzene-d6	294.5	113.9
11	Impinger	toluene-d8	293.8	112.1
11	Impinger	acrylonitrile-d3	305.0	115.2
12	Impinger	benzene-d6	390.0	130.0
13	Impinger	external	306.1	106.7
14	Impinger	1-3-butadiene-d6	335.9	118.2
14	Tedlar	isoprene	368.6	126.3
15	Impinger	isoprene	320.9	123.7
16	Tedlar	benzene-d6	312.7	92.0
16	Impinger	benzene-d6	312.7	92.0
17	Impinger	benzene-d6	271.3	87.2
17	Impinger	benzene-d6	240.5	81.2
18	Impinger	benzene-d6	147.0	41.3
19	Tedlar	benzene-d6	319.0	104.7
20	Impinger	benzene-d6	...	99.0
21	Impinger	isoprene	302.9	98.3
22	Impinger + XAD	benzene-d6	304.0	104.6
22	Impinger + XAD	toluene-d8	309.1	103.7
22	Impinger + XAD	acrylonitrile-d3	312.2	110.1

Overall data - Mean yield in µg/cig (CoV%)

Overall data (27 data sets)	319 (16)	108 (19)
Data from Tedlar bag (4 data sets)	262 (30)	91 (39)
Data from impinger trapping (23 data sets)	328 (12)	111 (15)
Impinger data calibrated with benzene (15 data sets)	327 (13)	111 (18)
Impinger data calibrated with toluene (4 data sets)	341 (13)	112 (10)
Impinger data calibrated with acrylonitrile (3 data sets)	306 (2)	108 (7)
Impinger data calibrated with isoprene (4 data sets)	316 (13)	110 (16)

laboratories for each of the five analytes studied, especially for low-yielding cigarettes such as 1R5F. Blank values in the table indicate that no third trap was used. Nine laboratories used two impingers and eight laboratories used three impingers in series. Laboratory 22 used a combination of two impingers and an adsorbent trap. Laboratory 16 participated in the trapping efficiency test with two impingers employed for one replicate but only used one impinger to generate data for the other 4 replicates in this study.

Laboratory 2 measured the amount of volatiles collected on the Cambridge Filter pad (CFP) and these values are given as trap 1 in Table 12. This laboratory also had the first impinger trap cooled to −4 °C and the second cooled to −70 °C. Volatile yields, with the exception of 1,3-butadiene, were not at the extremes of the range of yields given within this study even though their results gave a different trapping pattern to other laboratories who cooled each of their traps to the same low temperatures (−70 °C).

Laboratory 6 gave a different trapping pattern and gave extremely low 1,3-butadiene but extremely high acrylonitrile yields that were not related to this methodological feature. Laboratory 4 and 19 also gave slightly lower trapping efficiency for 1,3-butadiene in their first traps

Table 10. Comparisons of the rough estimates of mean yield, within-laboratory variability ('r') and among-laboratory variability ('R') from the 2006 and 2008 CORESTA Joint Experiments.

Statistic	Sample	1,3-Butadiene	Benzene	Toluene	Acrylonitrile	Isoprene
Mean [a]	2R4F - 2006	38.2	41.0	63.5	9.9	339.0
	3R4F - 2008	38.5	39.1	64.8	10.3	320.0
Within-laboratory variability 'r' [b]	2R4F - 2006	3.7	3.5	5.0	0.9	32.8
	3R4F - 2008	3.1	2.6	5.3	0.7	26.4
Among-laboratory variability 'R' [c]	2R4F - 2006	36.2	26.5	58.1	13.4	154.0
	3R4F - 2008	33.2	15.4	37.3	13.6	147.3
Mean	1R5F - 2006	11.6	12.3	16.7	2.6	109.0
	1R5F - 2008	12.7	13.1	17.8	3.3	109.0
Within-laboratory variability 'r'	1R5F - 2006	1.1	1.3	2.1	0.4	10.7
	1R5F - 2008	1.0	1.1	1.8	0.2	8.5
Among-laboratory variability 'R'	1R5F - 2006	11.7	9.1	16.7	5.1	56.0
	1R5F - 2008	9.8	6.2	12.2	9.1	58.9

[a] Mean = the average of the laboratory mean values, with each combination of laboratory and experiment regarded as separate laboratories for this and the statistics defined below.

[b] $r = 2 \{2\ Var(Rep)/5\}^{\frac{1}{2}}$, where Var(Rep) denotes the variance between replicate yields nested within laboratories and runs.

[c] $R = 2 \{2\ [Var(Lab+Run) + Var(Rep)/5]\}^{\frac{1}{2}}$, where Var(Lab+Run) denotes the sum of the variances between laboratories and between runs nested within laboratories.

Table 11. Comparisons of the differentiation between the two reference cigarettes for each selected volatile from the 2006 and 2008 CORESTA Joint Experiments.

Statistic	1,3-Butadiene		Benzene		Toluene		Acrylonitrile		Isoprene	
	2006	2008	2006	2008	2006	2008	2006	2008	2006	2008
All data										
CoV% of R(2R4F-1R5F)	101		69		91		139		50	
CoV% of R(3R4F-1R5F)		95		45		59		164		53
Matched data from 14 laboratories										
CoV% of R(2R4F-1R5F)	100		71		94		135		48	
CoV% of R(3R4F-1R5F)		110		48		66		189		70

Where CoV% of R(3R4F-1R5F) $=100 \{2\ [Var_{3R4F}(Lab+Run)+Var_{1R5F}(Lab+Run) + ((Var_{3R4F}(Rep)+Var_{1R5F}(Rep))/5)]^{\frac{1}{2}}\}/(Mean_{3R4F}-Mean_{1R5F})$

The extent to which each analyte was able to differentiate between 3R4F and 1R5F cigarette is shown.

- Values in the table which are ≥ 100 indicate that for the corresponding analytes it would not be possible to distinguish (with 95% confidence) between the cigarette types. For these analytes there would appear to be the greatest need to further investigate the causes of the laboratory methodology weaknesses.
- Conversely, for analytes whose values in the table are < 100, the 1R5F and 2R4F or 3R4F would be distinguished (with 95% confidence). However, substantial further work will still be needed to standardise the laboratory methods for those analytes positioned close to 100; perhaps those above 75.

compared to other laboratories. Laboratories 8, 11, 12, and 19 also reported lower trapping efficiencies for toluene in their first traps.

Results indicate that low temperature trapping from most laboratories gives high trapping efficiencies for organic volatiles. Therefore, laboratories with low trapping efficiencies should look to improve this aspect of their methodology. Results indicate that if trapping systems were constructed efficiently then two traps should be a sufficient number when proceeding to a standardised method.

Effects of the choice of internal calibration standards on smoke yields

In the light of experiences gained in the aromatic amine joint experiment (11) the question was raised whether the use of only one internal standard (IS) to measure the five targeted compounds was justified. The most variable data is generated by 1,3-butadiene and acrylonitrile that might be likely to react or evaporate over time in storage or during the methodological procedure. Therefore the use of an IS for each of these volatiles was investigated in this study.

Table 12. Impinger trapping efficiencies (in %).

Sample	Trap No.	Analyte	Laboratory (number of traps)																	
			2 (2)	3 (3)	4 (2)	5 (2)[a]	6 (2)	7 (2)	8 (2)	9 (3)	10 (3)	11 (3)	12 (3)	14 (3)	16 (2)	17 (3)	19 (2)	20 (2)	21 (3)	22 (XAD + 2)[b]
3R4F	1	1,3-butadiene	0.1	100.0	82.2	94.3	76.7	96.6	92.9	97.5	100.0	92.7	90.2	100.0	93.2	100.0	81.7		93.0	0.6
3R4F	2	1,3-butadiene	47.4	0.0	17.8	5.7	23.3	3.4	7.1	2.5	0.0	6.7	8.7	0.0	6.8	0.0	19.3		7.0	94.3
3R4F	3	1,3-butadiene	44.3	0.0	0.0					0.0	0.0	0.7	1.1	0.0		0.0			0.0	5.2
1R5F	1	1,3-butadiene	2.1	100.0	86.7	94.9	61.4	100.0	88.6	98.0	100.0	93.9	85.6	100.0	88.5	100.0	78.2		91.9	3.1
1R5F	2	1,3-butadiene	39.2	0.0	13.3	5.1	38.6	0.0	11.4	2.0	0.0	6.1	12.6	0.0	11.5	0.0	21.8		8.1	92.5
1R5F	3	1,3-butadiene	58.6	0.0	0.0					0.0	0.0	0.0	1.8	0.0	0.0	0.0			0.0	4.5
3R4F	1	benzene	0.0	100.0	96.6	97.5	94.8	100.0	87.0	95.8	100.0	90.4	92.3	98.9	100.0	100.0	97.2		91.3	53.6
3R4F	2	benzene	100.0	0.0	2.5	2.5	5.2	0.0	13.0	3.4	0.0	8.9	7.4	0.5	0.0	0.0	2.8		8.7	45.0
3R4F	3	benzene	0.0	0.0	0.9				0.0	0.8	0.0	0.8	0.3	0.5		0.0			0.0	1.4
1R5F	1	benzene	0.0	100.0	93.3	98.3	96.0	100.0	88.4	95.2	100.0	96.3	96.2	96.2	100.0	100.0	96.2	98.3	92.0	67.9
1R5F	2	benzene	100.0	0.0	3.6	1.7	4.0	0.0	11.6	2.8	0.0	3.7	3.8	3.8	0.0	0.0	3.8	1.7	8.0	31.3
1R5F	3	benzene	0.0	0.0	3.0				0.0	1.9	0.0	0.0	0.0	0.0		0.0	0.0		0.0	0.8
3R4F	1	toluene	0.2	100.0	96.1	93.3	89.8	98.3	71.8	94.3	100.0	78.4	81.7	99.1	100.0	100.0	87.9		92.0	92.9
3R4F	2	toluene	99.1	0.0	2.1	6.7	10.2	1.7	28.2	5.3	0.0	17.3	16.2	0.6	0.0	0.0	12.1		8.0	6.6
3R4F	3	toluene	0.6	0.0	1.8					0.4	0.0	4.3	2.1	0.3		0.0			0.0	0.4
1R5F	1	toluene	0.0	100.0	94.7	95.8	93.9	100.0	79.3	97.1	100.0	88.2	91.1	98.4	100.0	100.0	97.6		92.6	95.0
1R5F	2	toluene	99.1	0.0	2.8	4.2	6.1	0.0	20.7	2.2	0.0	10.4	8.1	1.0	0.0	0.0	2.4		7.4	5.0
1R5F	3	toluene	0.9	0.0	2.5					0.7	0.0	1.4	0.8	0.6		0.0			0.0	0.0
3R4F	1	acrylonitrile	0.0	100.0	96.6	98.4	65.8	100.0	88.7	99.2	100.0	90.6	94.8	100.0	100.0	100.0	98.6		92.3	16.1
3R4F	2	acrylonitrile	100.0	0.0	1.8	1.6	34.2	0.0	11.3	0.8	0.0	8.1	4.9	0.0	0.0	0.0	1.4		7.7	80.5
3R4F	3	acrylonitrile	0.0	0.0	1.6				0.0	0.0	0.0	1.3	0.3	0.0		0.0	0.0		0.0	3.4
1R5F	1	acrylonitrile	0.0	100.0	100.0	98.6	55.1	100.0	83.3	92.6	100.0	100.0	95.5	100.0	100.0	100.0	97.2		90.7	32.2
1R5F	2	acrylonitrile	100.0	0.0	0.0	1.4	44.9	0.0	16.7	7.4	0.0	0.0	4.5	0.0	0.0	0.0	2.8		8.3	64.2
1R5F	3	acrylonitrile	0.0	0.0	0.0				0.0	0.0	0.0	0.0	0.0	0.0		0.0			0.0	3.6
3R4F	1	isoprene	0.0	100.0	93.8	97.3	97.2	100.0	92.6	97.8	100.0	96.4	95.3	98.6	100.0	100.0	92.2		92.2	9.0
3R4F	2	isoprene	79.0	0.0	5.1	2.7	2.8	0.0	7.4	1.9	0.0	3.4	4.5	1.4	0.0	0.0	7.8		7.8	88.4
3R4F	3	isoprene	21.0	0.0	1.1				0.0	0.3	0.0	0.2	0.2	0.0		0.0			0.0	2.7
1R5F	1	isoprene	0.0	100.0	96.8	97.5	97.0	100.0	83.9	97.8	100.0	97.1	94.6	96.8	100.0	100.0	90.0	93.5	92.7	29.6
1R5F	2	isoprene	69.9	0.0	3.2	2.5	3.0	0.0	16.1	1.9	0.0	2.9	5.2	3.2	0.0	0.0	10.0	6.5	7.3	68.8
1R5F	3	isoprene	30.1	0.0	0.0				0.0	0.3	0.0	0.0	0.1	0.0		0.0			0.0	1.6

[a] Blank values indicate that no third trap was used.
[b] Remark - lab 22 used additionally a XAD-absorbent trap.

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For the Joint Experiment, it was requested that as many laboratories as possible should calibrate the targeted compounds against more than one IS to investigate the effect on their yields. Deuterated IS mixtures are commercially available and one such mixture (supplied by Restek) was circulated to participating laboratories who agreed to investigate this methodology aspect. Nine laboratories (Numbers 2, 3, 6, 9, 10, 12, 14, 16, 17, and 21) used this IS mixture (see Table 2).

The mean yields, using the different IS mixtures, are given in Tables 5–9. Visual inspection of these data and an analysis of variance revealed no statistically significant differences or directional trends in the mean yields based on the IS used. No consistent differences were found in the among-laboratory variability relating to calibration with different IS compounds or IS source.

Results suggest that one IS (particularly deuterated benzene or toluene) may be sufficient to calibrate the five selected volatiles when this methodology is taken towards standardisation.

Most of the laboratories used a linear calibration for the internal standards as shown in Table 2. Laboratory 1 used a quadratic calibration but was not associated with any particular extremes in yields.

Other potential factors influencing smoke yields

It is necessary to caution that the following observations should not be over-interpreted because like-for-like conditions are not being compared among laboratories. However, data may give some indication of the contribution of these factors to overall yields.

Comparison of impinger traps and tedlar bags for vapour phase collection

Up to four data sets were provided using Tedlar bag trapping and up to 29 data sets using impinger trapping based on the use of different calibration standards to produce the data set. Mean yields and variability are summarised in Tables 5–9. Although this is not a matched experiment, it appears that mean yields are very similar between the two methods. Yields from the Tedlar bags were slightly higher for 1,3-butadiene and toluene whereas other analytes tended to be slightly lower. However, there was also a higher associated variability between the four data sets for 1,3-butadiene.

Effect of Cambridge filter pads in the smoke collection set-up on smoke yields

The studied compounds are too volatile to trap on the CFP although Laboratory 2 had detected toluene there to a minor extent (0.6%). The mean yield data provided by the laboratories using impinger trapping and including (or not) the Cambridge Filter Pad (CFP) in the volatiles extraction was investigated. Table 1 indicates that Laboratories 2, 3, 4, 8, 10, 14, 16, 17, and 21 included and Laboratories 5, 6, 7, 9, 11, 12, 19, 22, and 23 did not include the CFP in such a way. As a test of the validity of excluding the CFP from the extraction stage, the mean toluene yields for the 1R5F and 3R4F cigarettes from each laboratory were determined

from all replicates averaged over all the different calibration standards studies. The mean toluene yields are taken from Table 6.

- Mean toluene yield *with* CFP = 68.2 µg/cig (3R4F) and 18.0 µg/cig (1R5F)
- Mean toluene yield *without* CFP = 63.6 µg/cig (3R4F) and 18.0 µg/cig (1R5F)

All laboratories used a CFP in their collection set-up, in many cases because the set-up is used to also measure some additional semi-volatiles in the procedure. These results alongside the small measured percentage of toluene trapping on the CFP would suggest that it is unnecessary to include the CFP in the extraction process.

Effect of various frit specifications in the impinger trap on smoke yields

Some laboratories had previously identified the frit specification as an important determinant of yield for certain analytes. The vapour phase of mainstream smoke is passed into the impinger trapping solution via a frit and the effect of a coarse or a fine specification was investigated. Some laboratory participants had previously found that this factor might particularly influence acrylonitrile and benzene data. However, these results indicate that this is not the cause of the wide variation in acrylonitrile yields. Table 1 shows that Laboratories 3, 5, 7, 9, 10, 14, 16, and 17 used a frit whereas Laboratories 2, 4, 6, 11, 12, 19, 21, and 22 did not use one. Laboratory 17 had exceptionally low benzene yields and therefore was excluded from the following analysis that is also shown in Table 7:

- Mean benzene yield *with* frit = 41.6 µg/cig (3R4F) and 13.8 µg/cig (1R5F).
- Mean benzene yield *without* frit = 41.1 µg/cig (3R4F) and 13.4 µg/cig (1R5F).

Results suggest that, within the overall among-laboratory variability, the presence or not of a frit did not significantly affect yields within the context of this among-laboratory study.

Effect of various impinger trap connections and tubing on smoke yields

Absorption of compounds on connecting tubing between traps and the use of certain tubing materials had been reported by certain laboratories as giving less absorption of smoke volatiles (e.g. high-density polyethylene). Table 1 indicates that Laboratories 2, 11, 20, and 22 used silicon tubing to attach trapping systems which had been identified as giving a particular problem with benzene absorption from experiences in some of the participating laboratories. However, Laboratory 20 did not produce benzene yield data for 3R4F.

- Mean benzene yields across 26 datasets = 39.4 µg/cig (3R4F) and 13.2 µg/cig (1R5F).
- Mean benzene yield for Laboratories 2, 11, 20 (1R5F only), and 22 using silicon tubing across 6 or 7 datasets = 37.6 µg/cig (3R4F) and 12.7 µg/cig (1R5F).

This limited information gives some indication but does not strongly support the preferred use of other tubing material. Several laboratories used glass tubing and one laboratory (No. 6) provided some extremely low yields which could be

due to leaks in their trapping system. Such aspects have been considered during other CORESTA method development for nicotine, NFDPM and CO collection and measurement in sidestream smoke (12, 13) that had recommended using polyvinylchloride (PVC) rather than rubber tubing connectors. Therefore, it would appear sensible that certain tubing types should be recommended in the final selected volatiles method.

Effect of the use of adsorbent traps on smoke yields

One laboratory (No. 22) used a combination of two impingers along with an XAD adsorbent trap. A comparison of the 3R4F yield data across each of the selected volatiles with that collected in three impingers by the same laboratory (No. 11) shows that the use of the adsorbent trap tends to increase the yields. However, the yields from the XAD trapping combination were not generally higher than the overall mean from all datasets. For 1R5F cigarettes, there was little difference in the overall mean and the yields given by this laboratory. This information would support using only glass impingers in a future standardised methodology for simplification purposes.

Effect of different dead volumes in the smoke collection system on smoke yields

Laboratories were requested to provide an estimation of the volume of the connecting tubing between the CFP holder and the surface of the trapping solvent in the impinger. The intention was to evaluate whether the range of connecting devices had a significant effect on yields. The highest dead volume (14 mL) in the collection system was associated with Laboratory 7 as identified in Table 1. This laboratory was not associated with the highest or lowest yields of any of the selected volatiles.

CONCLUSIONS

Similar yields were obtained when comparing data from Tedlar bag trapping with that from impinger trapping methods which is used by the majority of laboratories.
The use of an internal standard is standard practice for methodologies using mass selective detection. However, no significant effect was observed by applying different internal standards for calibration and therefore one internal standard, such as deuterated benzene, will be sufficient within a standardised methodology.
Some factors that should be incorporated in a standardised method include:

- Low temperature trapping that gives high trapping efficiencies within well constructed systems.
- Inclusion of two traps to provide sufficiently high trapping efficiency.
- Use of non-silicon connecting tubing for the traps to minimise adsorption and losses.

Even after these joint experiments, acrylonitrile and 1,3-butadiene yields are still extremely variable and the low or high levels are not easily explained from any of the parameters studied. The onus will be on those laboratories identified as giving extreme yields to look into this problem more deeply. Even so, this joint experiment undertaken by a large number of laboratories, the discussion of data and exchange of information within the Task Force has enabled the identification of those practices that will lead to a good recommended methodology. These findings will be carried forward to better construct a recommended method and determine among- and between-laboratory variability within collaborative studies. It is hoped that the high level of variability for acrylonitrile, isoprene and 1,3-butadiene will then be reduced to similar levels to those found for benzene and toluene.

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