Taskforce for the Determination of Total Triacetin in Charcoal Filters

Final Report February 2007

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Taskforce Objective: To develop a reference method for the determination of total triacetin in a charcoal on tow cigarette filter.

Background

Charcoal filters have been used for over 50 years and currently the global charcoal cigarette filter market is expected to increase significantly within the next few years.

There are two reasons for the production and usage of charcoal filters. Some smokers prefer charcoal filters for taste reasons. Charcoal filters are also well known to be highly efficient for the reduction of many volatile compounds from the vapour phase of cigarette smoke.

Cigarette and filter producers are well aware that the plasticiser content in a filter influences substantially the quality of a cigarette filter. Thus, a reliable, quick and accurate method for the determination of triacetin in charcoal filters could be one tool in the production of high quality charcoal cigarette filters. A CORESTA taskforce - Plasticisers in Filter Rod Production produced a reference method (CORESTA Recommended Method Number 59, published June 2004) for the measurement of triacetin in cellulose acetate filter rods using solvent extraction followed by gas chromatography and it was proposed to develop a similar method for the measurement of triacetin in charcoal filters.

Summary

Preliminary work by a number of taskforce members trying to measure the triacetin content of carbon filters using CRM number 59 had suggested that the recommended internal standard, anethole, was adsorbed by carbon and that the extraction efficiency from carbon filters was low. Thus the approach to developing a method for carbon filters was centered on:-

1) Finding an internal standard suitable for use with carbon (that is not adsorbed by carbon).
2) Investigating different extraction solvents.
3) Investigation of extraction time and technique.

A collaborative experiment was carried out using low (1mg/mm) and high (5mg/mm) loaded carbon filters with low and high triacetin levels. Thirteen laboratories tested these filter rods for levels of triacetin using solvent extraction followed by GC analysis. A range of solvents, extraction methods and internal standards were investigated. The results from the collaborative experiment allowed the taskforce to conclude:

1) The measured levels of triacetin in carbon filters were lower than the amount applied for the highly loaded carbon rods.
2) The measured amount of triacetin in carbon filters fell as the rods got older.
3) Little difference is seen in quantitative results between the different solvents used (methanol, ethanol and acetone).
4) The unsuitability of anethole as an internal standard (IS) was confirmed. Tripropionin (glycerol tripropionate CAS No 139-45-7) seemed to be a better internal standard (IS), however, some evidence indicated slight adsorption of the IS by carbon for the highly loaded carbon samples.
5) Further work using different solvents (carbon disulphide) and more aggressive extraction techniques *e.g.* soxhlet, heated extraction and accelerated solvent extraction failed to give complete recovery of the triacetin from the high loaded carbon rods.

The main problem to be solved seemed to be that some of the applied triacetin was remaining locked in the pores of the carbon so that it was not completely extracted. However, it was well known that triacetin slowly hydrolyses initially into glycerol diacetate and acetic acid and then into the glycerol monoacetate and further acetic acid. Complete hydrolysis would reduce the triacetin to glycerol. The presence of water and alkaline conditions accelerate the hydrolysis and the inner surface of carbon can provide moist alkaline conditions. If all the triacetin on the carbon had hydrolysed then the extraction was measuring all of the remaining triacetin and not the hydrolysate, but if some triacetin remained on the carbon as triacetin then the extraction was incomplete and the analysis was not measuring total triacetin in a charcoal on tow cigarette filter, the objective of the taskforce.

A large amount of work was done to attempt to conclusively measure the nature of the material remaining on the carbon. This was carried out using two techniques; the first by measuring all decomposition products of triacetin and attempting to calculate the original amount from these and the second involving thermal desorption in an inert gas stream or under vacuum and measuring the eluted material using GC-MS. The studies looking at the hydrolysis products measured glycerol diacetate, glycerol

monoacetate, glycerol and acetic acid. Quantification of the levels of these materials broadly accounted for the triacetin initially applied. However, some of the thermal desorption procedures did detect (but not quantify) low levels of triacetin in the carbon. It was obvious that the triacetin did hydrolyse in the presence of carbon and that levels of triacetin measured by simple solvent extraction would decrease as the rods aged or as carbon loading increased. Therefore, any method developed by the taskforce relying on the measurement of triacetin only would underestimate the amount of triacetin on the carbon filters and give a different answer depending on the age the filters that could not be related to the initial application level. The taskforce concluded that the objective could not be met and a technical report should be produced detailing the work carried out.

The majority of work carried out used an extraction time of three hours, however, a study carried out suggested that much longer extraction times could give complete recovery of the total acetins (see the minutes of meeting 4). In this work filters were extracted for periods of up to one week. The total acetins increased for the carbon samples the longer they were extracted. For collaborative sample number 4 (high carbon and high plasticiser) even after seven days of extraction the measured values were still increasing slightly. If the extraction time was allowed to go on for considerably longer the recovery would be expected to increase for the carbon containing filters. After seven days extraction an average recovery value for six replicate determinations of 93.5% was found. As longer extraction times would be expected to give higher recoveries within the error of measurement of both target and recovery values the actual recovery may be 100%.

Another approach to estimating the recovery is to use a model system although this may be more representative of fresh rather than aged rods. A study of this type was carried out by adding exactly known amounts of solvent, cellulose acetate, triacetin and carbon at two different levels (equivalent to 60 mg/cigarette and 120 mg/cigarette). If only triacetin was measured recoveries of 98.5% (100% within experimental error) for the sample without any carbon and 76 and 64% for the two different levels of carbon containing samples were given. If, however, total acetins are measured recoveries for all samples are 100% within experimental error.

The conclusions were definitive that the incomplete recovery of triacetin by extraction is mainly due to the decomposition of triacetin on storage in carbon containing rods. Very low levels of triacetin may have also remained strongly adsorbed on the carbon surface.

Collaborative Experiments

For the first collaborative experiment a series of 5 filter samples were produced as detailed in Appendix 2. These samples were to cover a range of carbon loading and triacetin levels. The experiment also included a monoacetate control. Samples were distributed to all participating laboratories and analysed according to the protocol given in Appendix 3. The results of the first round of testing are given in table 1 below. All triacetin values are expressed as mg/rod.

Table 1. Results of the First Collaborative Experiment

Sample ID	**1**	**2**	**3**	**4**	**5**
Sample Properties	**LC LPz**	**LC HPz**	**HC LPz**	**HC HPz**	**Control**
Expected Triacetin	***19.5***	***54.6***	***18.1***	***53.3***	***44.3***
Solvent Ethanol					
FTC	17.12	50.64	10.24	35.20	45.89
BAT Germany	19.57	57.27	12.57	39.77	46.65
Celanese Acetate Narrows, VA	21.00	60.13	13.44	43.73	46.66
Imperial Tobacco Hamburg	23.13	58.15	14.44	41.59	46.82
Rhodia	20.29	57.17	13.35	40.21	43.81
Japan Tobacco Inc.	21.35	57.72	12.68	40.36	46.60
Eastman Chemical Company	21.16	56.57	13.57	37.29	46.32
Acetate Products*	20.23	57.94	13.85	42.35	44.96
Hauni	18.44	49.94	12.46	35.72	41.29
RJR	19.52	56.99	12.42	39.33	43.94
KTG	19.75	57.35	13.08	40.75	45.19
BAT Southampton	18.24	55.38	13.11	39.57	46.89
PT HM Sampoerna Tbk.	19.05	57.66	9.29	35.51	45.61
Mean	**19.91**	**56.38**	**12.65**	**39.34**	**45.43**
Standard Deviation	***1.56***	***2.90***	***1.42***	***2.69***	***1.63***
%CV	***7.83***	***5.15***	***11.22***	***6.83***	***3.58***
Max	***23.13***	***60.13***	***14.44***	***43.73***	***46.89***
Min	***17.12***	***49.94***	***9.29***	***35.20***	***41.29***
	* Note different ISD used (glycerol tributyrate)				
Solvent Methanol					
FTC	16.22	50.58	10.88	38.65	38.92
Imperial Tobacco Hamburg	19.93	57.00	14.44	41.67	46.20
Mean	**18.07**	**53.79**	**12.66**	**40.16**	**42.56**
Standard Deviation	***2.62***	***4.54***	***2.52***	***2.14***	***5.14***
Solvent Acetone					
FTC	20.29	59.06	12.00	40.02	47.82
Imperial Tobacco Hamburg	21.11	56.89	12.78	41.06	45.22
# BAT Germany	19.67	58.36	12.87	40.72	46.75
Mean	**20.35**	**58.10**	**12.55**	**40.60**	**46.60**
Standard Deviation	***0.72***	***1.11***	***0.48***	***0.53***	***1.31***
	# Note 30 min extraction time (shaking)				

KEY : LC LPz = low carbon, low triacetin LC HPz = low carbon, high triacetin
HC LPz = high carbon, low triacetin HC HPz = high carbon, high triacetin

The samples were up to two months old at the time of the first analysis. A summary of this data is given in table 2 below. Again all triacetin values are expressed as mg/rod.

Table 2. Summary Results of the First Collaborative Experiment

	LC LPz	LC HPz	HC LPz	HC HPz	Control
Expected Triacetin	**19.5**	**54.6**	**18.1**	**53.3**	**44.3**
Solvent Ethanol	19.9	56.4	12.7	39.3	45.4
Solvent Methanol	18.1	53.8	12.7	40.2	42.6
Solvent Acetone	20.4	58.1	12.5	40.6	46.6

The foremost conclusion from this work seemed to be that for the high carbon loaded samples not all the triacetin was being extracted from the filter rod. As an immediate confirmation and to access the effects of ageing of the samples the rods were retested and the data is shown in table 3 below.

Table 3. Effect of Ageing

Sample ID	**1**	**2**	**3**	**4**	**5**
Sample Properties	**LC LPz**	**LC HPz**	**HC LPz**	**HC HPz**	**Control**
Expected Triacetin (mg/rod)	***19.5***	***54.6***	***18.1***	***53.3***	***44.3***
Mean first test (13 labs)	19.9	56.4	12.7	39.3	45.4
Mean second test (6 labs)	18.5	55.3	10.1	35.2	44.7

Samples produced early March 2005
First test late April to May 2005
Second test December 2005

This data can also be expressed in terms of triacetin percentage recovery and is shown in table 4 below.

Table 4. Percentage Recoveries

Sample ID	**1**	**2**	**3**	**4**	**5**
Sample Properties	**LC LPz**	**LC HPz**	**HC LPz**	**HC HPz**	**Control**
% Recovery first test	102	103	70	74	103
% Recovery second test	95	101	56	66	101

The results confirmed the low measured values for the high loaded carbon samples and that as the samples aged the measured value was reduced. The data from the monoacetate control suggested that even for aged rods without carbon triacetin could be fully extracted and measured. Further work with a new sample of intermediate carbon loading, 3 mg/mm, also showed that complete extraction was not achieved. The average measured value for triacetin being 30.4 mg/rod for rods with an expected triacetin value of 39.5 mg/rod.

Internal Standards

An internal standard is usually a stable compound that is available in a pure form and is chemically similar to the analyte of interest. Internal standards are used to correct for any loss of analyte during sample extraction, preparation or analysis. The internal standard should provide a signal that is similar to the analyte signal in most ways but sufficiently different so that the two signals are readily distinguishable by the analytical instrument.

When performing extractions with activated carbon in the extraction mix one of the main potential problems was adsorption of the internal standard from solution giving an artificially low internal standard area count and therefore an artificially high sample value?

Previous work had shown that anethole the internal standard recommended in CRM number 59 was adsorbed by carbon but that tripropionin when used at the recommended concentration (3 g/L) did not show any significant adsorption on to carbon when the carbon weight was less than 200 mg per 20 ml of solvent. At higher carbon weights adsorption was observed.

The recommended procedure for the collaborative experiment (see Appendix 3) was extraction of 3 rods with 200 ml of solvent so that for the high loaded carbon rods the carbon would have been present at 162 mg per 20 ml which is below the level for adsorption to occur. (Note this is for coconut shell carbon which is commonly used in cigarette filters with a surface area approximately 1100 m^2/g, for higher surface area/activity carbons it is probable that internal standard adsorption would occur at lower carbon weights).

Using the results from the collaborative experiment an attempt was made to assess if any adsorption of the tripropionin internal standard had occurred. This was quite difficult due to the very different GC systems used by the different laboratories giving widely different internal standard area counts. To allow comparison the internal standard peak area of the sample with carbon was expressed as a percentage of the internal standard peak area without carbon.

A value of 100% should indicate no adsorption and values below 100% indicate that adsorption had occurred. The only solvent that a significant number of laboratories had used was ethanol for which the data is shown in table 5 below.

Table 5. Internal Standard Percentage Peak Area's

Laboratory Number	Carbon Sample IS Peak Area as % of Control IS Peak Area			
	LC LPz	**LC HPz**	**HC LPz**	**HC HPz**
	Carbon 33 mg/20 ml of solvent		Carbon 162 mg/20 ml of solvent	
1	107	107	98	100
2	100	100	97	97
3	98	98	95	96
4	96	94	93	93
5	91	89	100	89
6	104	102	97	100
7	104	104	99	99
8	104	104	99	99
9	72	87	55	65
10	102	102	96	98
11	101	100	98	99
Mean All Labs	**98**	**99**	**93**	**94**
Mean Lab 9 omitted	**100**	**100**	**97**	**97**

The data tends to suggest that at the lower carbon loading no significant adsorption of the internal standard occurs. At the higher carbon loading it may be that slight adsorption of the internal standard could have occurred but it does seem that for up to about 200 mg of carbon per 20 ml of solvent that tripropionin can be used as an internal standard for extraction of samples containing carbon.

One laboratory used an alternative internal standard namely glycerol tributyrate. For this internal standard when using ethanol as solvent the average percentage internal standard peak area values for the low loaded carbon samples was 92% and for the high loaded carbon samples was 82%. Although it is difficult to draw firm conclusions from one set of data it would appear that this internal standard suffered more adsorption by the carbon than tripropionin.

As a rule for any work involving activated carbon in the extraction mixture it is prudent to perform confirmatory experiments under the exact conditions of the analysis to be carried out to ensure the suitability of internal standard to be used before commencing any measurements.

Extraction Solvents

Four extraction solvents were investigated by the taskforce members. Initially three solvents were used, ethanol, methanol and acetone as these were all regularly used by the participating laboratories. After the initial collaborative experiment other solvents were suggested that may give better extraction such as carbon disulphide, acetonitrile and chloroform but only carbon disulphide was used to test for extraction efficiency. A summary of the data for the different extraction solvents used in the initial collaborative is shown in table 6 below.

Table 6. Values for Different Extraction Solvents

Expected Triacetin (No. of labs)	LC LPz	LC HPz	HC LPz	HC HPz	Control
	19.5	54.6	18.1	53.3	44.3
Ethanol (13)	19.9	56.4	12.7	39.3	45.4
Methanol (2)	18.1	53.8	12.7	40.2	42.6
Acetone (3)	20.4	58.1	12.5	40.6	46.6
Carbon Disulphide (1)	19.5	57.0	12.4	39.3	43.9

The data in the table tends to suggest little difference between the solvents as far as extraction of triacetin from the filter rods is concerned. (Note that the differences in recoveries across the extraction solvents may also be due to the different number of laboratories that analysed each solvent type).

However, it was reported that the alcohol based solvents showed greater degrees of degradation of triacetin and the tripropionin internal standard when compared to acetone or carbon disulphide. This was attributed to alkaline material from the carbon promoting hydrolysis in the alcohol solutions. Even for the three hour extraction time used an increase in the levels of triacetin breakdown products, glycerol diacetate and glycerol monoacetate in filter rod extracts was observed in the alcoholic solvents.

Longer term storage exacerbated these effects. Even though the extraction efficiency of the solvents seems to be similar care would be required when selecting a solvent to ensure that the solvent did not cause degradation of the triacetin during the extraction time employed or during storage of calibration solutions.

Sample Extraction Time and Temperature

CORESTA recommended method (number 59) for the determination of triacetin in acetate filter rods recommended an extraction time of three hours. The majority of work done by the taskforce used an extraction time of three hours for the measurement of triacetin in carbon filters. Some work was done looking at different extraction times and temperatures. The conclusion of this work was that at room temperature a maximum level of measured triacetin was given after extraction times of 2 to 3 hours.

At higher temperatures (55°C) the extraction time seemed to be shorter and a maximum extraction could be obtained in about 1.5 hours. For filters with lower levels of carbon complete extraction was also observed at shorter times. At room temperature a minimum of two hours was required for maximum extraction with the highest carbon level used, an extraction time of three hours was thus confirmed by this work.

Extraction Methods

For the extraction of filter rods the procedure was to take the rods and slit them longitudinally. Each rod was then cut into approximately equal segments of minimum 10 mm and maximum of 20 mm length. The rod segments were then placed in to a flask and the extraction solvent added.

The most used extraction method was to shake the flasks for three hours using a flask shaker. As the major problem encountered by the taskforce was lower than expected triacetin values thought to be caused by incomplete extraction of the triacetin other extraction techniques were tried.

These included soxhlet extraction, microwave extraction, ultra sonic extraction and accelerated solvent extraction. None of these procedures gave higher levels of extraction than shaking.

Effect of Sample Age

Due to the necessity to distribute samples globally to the laboratories concerned all the samples used for collaborative testing had aged for several weeks before testing. Some data was presented that suggested for fresh samples (taken immediately from the filter production machine) tested immediately after production extraction efficiencies approaching 100% could be achieved. But that even after relatively short sample ageing (hours) the measured triacetin value decreased.

The Interaction of Triacetin and Carbon

All of the work done by the taskforce showed that for the higher carbon loaded rods the measured triacetin values were lower than the levels applied during manufacture and that the measured levels reduced as the filter rods aged. The level of triacetin recovery decreased as the amount of carbon in the filter increased. Considerable effort was therefore given to trying to determine what had happened to the triacetin that was apparently not extracted from the rod. Was it present as triacetin on or in the carbon, or had it hydrolysed giving a mixture of hydrolysis products – glycerol diacetin, glycerol monoacetin, glycerol and acetic acid.

All of the testing carried out by the taskforce showed that hydrolysis of triacetin had occurred and glycerol diacetin, glycerol monoacetin and acetic acid could be detected on the filter rods with higher levels being evident on the filter rods of higher carbon loading. Evidence was also seen of small levels of glycerol in the filter rods. Initial attempts were made to calculate the amount of triacetin in the filter rods from the measurement of acetic acid concentration but these were not successful as the extent of hydrolysis (triacetin to glycerol diacetin plus one unit of acetic acid or to glycerol monoacetin plus two units of acetic acid or to glycerol plus three units of acetic acid) was not clear.

Values based on assuming that one unit of acetic acid was produced per unit of triacetin gave overestimates of the amounts of triacetin which supported the experimental observations that glycerol monoacetin and glycerol were present in the filter rods. Further work was carried out involving the measurement of all the possible hydrolysis products. For the high carbon samples the sum of the glycerol

mono-, di-, and triacetates did not completely match the expected triacetin levels and there was excess acetic acid not explained by the glycerol mono- and di-acetates.

The complete hydrolysis of some triacetin to glycerol would explain most of the remaining discrepancy. It would appear that the incomplete recovery of triacetin is largely due to the hydrolysis of triacetin on storage in carbon containing rods. Work on this technique was slightly complicated by the fact that no commercial materials were available to use for calibration standards for the glycerol diacetin and glycerol monoacetin. A large amount of work therefore had to be carried out to experimentally determine the GC response factors for glycerol diacetin and glycerol monoacetin. Also external standards were used to ensure that adsorption of material by carbon did not affect the measured values.

Thermal desorption and porosity experiments were also used to try to identify any material remaining on the carbon after solvent extraction. Carbon was removed from the high plasticiser high carbon rods and washed in acetone for three hours to remove the 'extractable' triacetin portion. Porosity measurements were then made on the acetone washed carbon from the filter rods, the acetone washed material after out gassing at 425°C under vacuum and on fresh carbon that had not been used in filter production.

These tests showed that the carbon from filter rods prior to out gassing had the lowest porosity and that out gassing improved the porosity but did not restore it to the level of the fresh carbon. This suggested that even after out gassing some material remained in the pores of the carbon reducing its porosity. Further samples of the extracted acetone washed carbon were tested using thermal desorption and GC-MS. The acetone washed carbon removed from the filter rods was divided in to two samples one of which was powdered. Both of these samples were thermally desorbed at temperatures up to 350°C under helium flow and the eluted compounds were analysed by GC-MS. For both samples detectable, but not quantifiable, amounts of triacetin, glycerol diacetin and acetic acid were found. This may suggest that some probably very minor levels of triacetin remained as triacetin, strongly adsorbed in the pores of the carbon even for filter rods that were over one year old.

Appendix 1 Taskforce Members

Bill Coleman - RJRT
Bill Deaton - Lorillard Tobacco Co.
Brian Webster - Acetate Products
Christian Schultz - Imperial Tobacco
Diah Prasetyaningrum - PT HM Sampoerna Tbk
Eckart Schutz - Rhodia Acetow
Hasegawa Takashi - Japan Tobacco
Henning Moller - Hauni
Hiroshi Shibuichi - Japan Tobacco
Jack Hensley - Eastman Chemical Company
Joanne Walker - Filtrona (Secretary)
John Newbury - Eastman Chemical Company
Jong Yeol Kim - KT & G Central Research Institute
Karl Thelen - Wattens (Scientific Commission Liaison)
Lance Deutsch - Celanese Acetate
Larry Renfro - Eastman Chemical Company
Linda Crumpler - RJRT
Ludwig Riepert - Imperial Tobacco
Maria Cashmore - BAT Southampton
Mike Taylor - Filtrona (Co-ordinator)
Mochammad Sholichin - PT HM Sampoerna Tbk
Peter White - BAT Southampton
Ray Robertson - Celanese Acetate
Robert Eberhardt - Rhodia Acetow
Soo-Ho Kim - KT & G Central Research Institute
Steve Herod - Acetate Products
Ulf Boderius - BAT Germany
Valerie Troude - Altadis
Yang Huawu - Changsha Cigarette Factory

Appendix 2 Filters Produced for Collaborative Experiment

The filters for the collaborative experiment were all 108 x 24.35 mm with a pressure drop of 400 mm WG wrapped in standard plugwrap. The details of triacetin and carbon loading are given in table 7 below.

Table 7. Filter Rods for the First Collaborative Experiment

Sample Description	Triacetin %	Triacetin mg/rod	Carbon mg/mm	Carbon mg/rod
LC LPz	3	19.5	1	108
LC HPZ	10	54.6	1	108
HC LPz	3	18.1	5	540
HC HPz	10	53.3	5	540
Control	7	44.3	None	None

Appendix 3 Collaborative Experiment Protocol

1. REFERENCES

1.1. ISO 3402:1999, Tobacco and tobacco products – Atmosphere for conditioning and testing.

1.2. CRM59 - CORESTA Recommended Method No. 59

1.3. Minutes of the 1st Taskforce Meeting 'Triacetin in Carbon Filters', Thursday January 27th 2005, Kenilworth, UK.

2. PRINCIPLE

2.1. Triacetin is extracted from filter material by shaking in a solvent however certain variables of the extraction technique (solvent type, extraction time and method) will be investigated by designated laboratories (see section 8.). The triacetin concentration of the extract is determined by using gas chromatography. Results are expressed as the weight of triacetin per filter rod (mg/rod).

Note: Triacetin percentage can be calculated if the weights of all other rod components are known and quantified.

3. APPARATUS

3.1. A gas chromatograph preferably equipped with a flame ionisation detector, (however other appropriate detectors can be used) and with an integration unit (or data handling unit). Analysis can be carried out on packed or capillary columns. Examples of suitable GC columns are given below.

DB-1 (100% DiMe-Polysiloxane),
DB-5 (5% Ph-Polysiloxane),
SIL-CP-19 (19% CNPropyl-Polysiloxane),
DB-Wax (PEG),
HP-5 (Cross linked 5% Ph Me Siloxane) (30m, 0.53mm i.d., 0.5µm).

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3.2. A standard laboratory flask-shaking machine.

3.3. The necessary general laboratory equipment, for the preparation of samples, standards and reagents. All laboratory equipment should be glass.

3.4. A suitable conditioning environment to ensure compliance with ISO 3402.

4. REAGENTS

4.1. *Ethanol (96%):* analytical grade (for those laboratories applicable, methanol and acetone both of analytical grade)

Note: Denaturing agents should be identified on the results sheet and should not cause any interfering signals in the chromatogram.

4.2. *Internal Standard:* Glycerol Tripropionate CAS 139-45-7 (minimum purity 99 %.) Concentration in extraction solvent 3.0g/L. Internal standard should be stored as recommended by the manufacturer.

4.3. *Gases:* Carrier and auxiliary gases necessary for the operation of the gas chromatograph.

4.4. *Triacetin:* Used for the preparation of standard solutions (minimum purity 99%)

4.5. *Extraction Solvent:* 200mL of ethanol (or methanol or acetone) described in sections 4.1 & 4.2 containing 3.0g/L of the internal standard glycerol tripropionate.

5. STANDARDS

Dissolve triacetin in the appropriate solvent described in section 4.5 to produce a series of at least four calibration solutions with equidistant concentrations. Standard solutions containing 0, 1, 2, 3 mg triacetin per ml of extraction solvent should meet the above requirement when 3 rods are extracted with 200 ml of extraction solvent. A standard of "0%" should be included into the sequence in order to see any contamination of triacetin in the extraction solvent.

6. PROCEDURE

6.1. *Gas Chromatography*

Ensure the solvent, internal standard, triacetin and other component peaks are baseline separated. Examples of suitable GC conditions for a DB wax column are given below.

GC
Standard GC equipped with an auto sampler

Injector
Injection Volume 1µl

Inlet
Type Split/Split less
Mode Split
Temperature 250°C
Pressure 0.97bar
Gas Type Helium
Split Ratio 5:1
Split Flow 87.8ml/min
Total Flow 108.4ml/min

Inlet liner:
Split liner packed with deactivated fused silica or glass wool according to the GC manufacturer's recommendations

Oven
Initial Temperature 120°C (initial time 0 min)
Rate 10°C/min
Final Temperature 230°C (hold 5 min)

Detector
Type FID
Temperature 250°C
Make-up-Gas Nitrogen
Make-up-Flow 5 ml/min
Hydrogen Flow 40 ml/min
Air Flow 300 ml/min
Range 0

Column
Type Fused Silica, 30m x 0.53mm i.d.
Supplier J & W
Stationary Phase DB-Wax
Film Thickness 1µm
Flow 17.6ml/min @ 120°C

Cycle Time 16min

6.2. *Calibration of the Gas Chromatograph*

Inject duplicate aliquots of the standard solutions into the gas chromatograph.

Record the peak areas of the triacetin and internal standard. Calculate the ratio of the peak areas for triacetin to the internal standard. Establish the calibration graphs between the area ratios and the triacetin concentrations. Calculate the linear regression parameters.

6.3. *Calibration check*

A full calibration procedure should be carried out prior to sample analysis using the prepared standard solutions described in section 5.

To check calibration use an independently prepared standard after every 10 sample vials. If the value for this solution differs by more than ±3% from the original calibration value the full calibration must be repeated.

6.4. *Filter rod sample preparation*

Conditioning: Condition the filter rods for a minimum of 24 hours under the environment specified in ISO 3402.

Filter rod preparation: Take 3 rods and slit them longitudinally. Cut each rod into approximately equal segments of minimum 10 mm and maximum of 20 mm length. Place rod segments including the plug wrap paper in a 500 ml Erlenmeyer flask. Add 200 ml of extraction solvent, as described in section 4.5., with a pipette (or similar precision delivery device). Seal the top of the flask securely.

Extraction: Ten extractions should be carried out on each filter type. The prepared flask is placed on a flask shaker for 3 hours. After shaking is complete, transfer an aliquot of the solutions to vials for testing on the gas chromatograph with each extract injected twice.

6.5. *Measurement and calculation*

Inject duplicate aliquots of each extraction into the gas chromatograph. For each injection record the peak areas of triacetin and of the internal standard. Calculate the ratio of the peak area of triacetin to that of the internal standard. Using the calibration procedure produced in section 6.2 determine the concentration of triacetin in the extraction solution as mg/ml. Ensure that values lie within the range of standards prepared in section 5. Calculate the triacetin content in mg/filter rod as described in section 7 and report the mean to the nearest 0.1 mg.

7. CALCULATION OF TRIACETIN

7.1. The linear equation of the calibration of the GC (described in section 6.2) should be used for calculating the concentration of triacetin in the extraction solution.

$$C = \frac{Y - B}{A}$$

C: concentration of triacetin in the extraction solution (mg/ml)
Y: ratio of the peak areas of triacetin and internal standard in the chromatogram
B: y-axis intercept of the linear regression line (calibration curve)
A: slope of the linear regression line (calibration curve)

$$\text{mg triacetin per filter rod (mg/rod)} = \frac{C \times V}{Z}$$

V: volume of solvent used for extraction (ml)
Z: number of filter rods used for extraction

For informational purposes, the mean weight of the rods may also be reported.

8. OPTIONAL EXTRA MEASUREMENTS

An attempt should be made to measure any degradation products such as glycerol diacetate and glycerol monoacetate wherever possible.

All collaborators are free to carryout any additional measurements and report their findings on the spreadsheet, however the following additional investigative work has been proposed (for full details refer to 'Minutes of the 1st Taskforce Meeting – Triacetin in Carbon Filters', Thursday January 27th 2005, Kenilworth, UK);

Extraction time variation	-	Linda Crumpler, RJRT Robert Eberhardt, Rhodia Joanne Walker, Filtrona
Extraction method	-	Ray Robertson, Celanese (boiling) Linda Crumpler, RJRT (water bath) Joanne Walker, Filtrona (ultrasonic)
pH of extraction solution	-	Ulf Boderius, BAT Germany
Adsorption of internal standard by different activity carbon	-	Maria Cashmore, BAT Southampton & Joanne Walker, Filtrona

9. DATA COMPLIATION

All data should be returned to the secretary (Joanne Walker) by the end of May 2005. The identified high priority sample (Filter No. 4) shall wherever possible be analysed during the 25th April to 6th May 2005 time window, with exact dates noted on the results sheet. Any other deviations should be noted on the results sheet. All additional data generated should be recorded on in the spreadsheet with additional sheets copied directly from the original.

Attachments

Appendix 4 – Minutes of the first meeting of the taskforce determination of total triacetin in charcoal filters – 27 January 2005, Kenilworth UK.

Appendix 5 – Minutes of the second meeting of the taskforce determination of total triacetin in charcoal filters – 8 September 2005, Stratford upon Avon, UK.

Appendix 6 – Minutes of the third meeting of the taskforce determination of total triacetin in charcoal filters – 7 February 2006, Newcastle upon Tyne, UK.

Appendix 7 – Minutes of the forth meeting of the taskforce determination of total triacetin in charcoal filters – 20 October 2006, Paris, France.