

Measurement of alkyl 2-cyanoacrylates at low concentrations

Further work

Prepared by the **Health and Safety Laboratory**
for the Health and Safety Executive 2008

Measurement of alkyl 2-cyanoacrylates at low concentrations

Further work

Matthew Coldwell BSc
Health and Safety Laboratory
Broad Lane
Sheffield
S3 7HQ

This report describes research into improved cyanoacrylate sampling methods. The research was an assessment of Automated Thermal Desorption (ATD) as an alternative sampling/analytical technique for the measurement of airborne cyanoacrylate and the development of modified Tenax sampling tubes.

HSE introduced the 0.3 ppm Short-term exposure limit (STEL) in 2000 for both ethyl-2-cyanoacrylate (ECA) and methyl-2-cyanoacrylate (MCA). These limits were transposed into Workplace Exposure Limits (WELs) in 2005, with revised compliance criteria. HSL investigated the ability of existing sampling methods to test compliance with the limit and found significant errors. Sampling losses are apparently due to polymerisation on the glass wool plug of the Tenax tube used for sampling.

Eleven types of modified Tenax tube were prepared and evaluated at 0.03 ppm using a dynamic standard atmosphere. Analysis was by High Performance Liquid Chromatography (HPLC) with Ultra-Violet (UV) detection. Two tubes were found to compare well with the impinger based reference method. One tube replaces the front wool plug with a steel mesh and polypropylene o-ring to hold the sorbent in place. The other tube is treated with a phosphoric acid solution. Both tubes were subjected to a thorough laboratory validation, using BS EN482 as guidance. The steel mesh/o-ring tube performed slightly better than its counterpart when sampling MCA atmospheres and hence is the preferred choice. This tube is capable of providing reliable and sensitive measurement of cyanoacrylate atmospheres across a range of concentration, temperature and humidity.

This report and the work it describes were funded by the Health and Safety Executive (HSE). Its contents, including any opinions and/or conclusions expressed, are those of the author alone and do not necessarily reflect HSE policy.

© Crown copyright 2008

First published 2008

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means (electronic, mechanical, photocopying, recording or otherwise) without the prior written permission of the copyright owner.

Applications for reproduction should be made in writing to:
Licensing Division, Her Majesty's Stationery Office,
St Clements House, 2-16 Colegate, Norwich NR3 1BQ
or by e-mail to hmsolicensing@cabernet-office.x.gsi.gov.uk

ACKNOWLEDGEMENTS

The authors would like to thank CSD3 (formerly TD3) of HSE for supporting this work.

CONTENTS

1	INTRODUCTION.....	1
2	EXPERIMENTAL TECHNIQUES	2
2.1	Standard atmospheres.....	2
2.2	Sampling methods.....	3
2.3	Silanisation of glassware.....	3
3	AUTOMATED THERMAL DESORPTION (ECA only).....	4
3.1	System.....	4
3.2	Standard solutions.....	4
3.3	Experimental and discussion.....	4
4	HIGH PERFORMANCE LIQUID CHROMATOGRAPHY	6
4.1	System.....	6
4.2	Standard solutions.....	6
4.3	Experimental and discussion.....	6
5	METHOD VALIDATION.....	10
5.1	Validation criteria.....	10
5.2	Results and discussion.....	10
5.3	Short term storage trials	12
5.4	Limits of detection	13
6	CONCLUSIONS.....	14
7	REFERENCES.....	15
8	APPENDICES	16

EXECUTIVE SUMMARY

Objectives

To assess the viability of measuring airborne ethyl 2-cyanoacrylate (ECA) and methyl 2-cyanoacrylate (MCA) by pumped sampling onto Tenax automated thermal desorption (ATD) tubes and subsequent analysis by ATD with gas chromatography employing mass spectrometric detection (GC/MS).

To evaluate different modified glass Tenax tubes for the sampling and measurement of ECA and MCA to comply with short term exposure limits (STEL). Solvent desorption followed by High Performance Liquid Chromatography (HPLC) would be used for sample analysis.

Validate the most appropriate method(s) for the sampling and analysis of ECA/MCA using BS EN 482 as guidance.

Main Findings

ATD does not appear to be suitable for the analysis of ECA/MCA samples taken onto Tenax ATD tubes.

Eleven different modified glass Tenax tubes were investigated. Two designs of tube, one phosphoric acid treated, the other using a steel mesh and polypropylene o-ring in place of glass wool plug, were found to give good recoveries and to be robust during sampling. The phosphoric acid treated tube is easier to prepare than its counterpart

Validation of both types of modified glass Tenax tubes followed by HPLC analysis has been carried out using BS EN 482 as guidance. Performance of the steel mesh/polypropylene o-ring Tenax is marginally better for sampling MCA providing lower overall uncertainties. Caution needs to be exercised when sampling in atmospheres of high temperature and humidity.

A total of 93 standard atmosphere runs were performed.

Main Recommendations

Airborne cyanoacrylates can be sampled using either of the modified glass Tenax tubes, subsequent analysis by HPLC is both reliable and sensitive. The authors recommend the sampling tube with steel mesh and polypropylene o-ring.

Consideration should be given to a small field trial prior to full scale adoption of the new method.

Attempts should be made to establish commercial production of one or both the modified glass Tenax tubes.

1 INTRODUCTION

Alkyl 2-cyanoacrylates (ACAs) are widely used as adhesives. Ethyl 2-cyanoacrylate (ECA) is the most widely used both in industrial and domestic applications, methyl 2-cyanoacrylate (MCA) is also used in industry although its use is in decline over recent years due to its more pungent odour.

Both ECA and MCA are irritating to the skin, eyes and respiratory system. HSE has already carried out research into the sampling and analysis of cyanoacrylates (Keen and Pengelly, 1996 & Griffiths, 2000) and has recently introduced a 0.3 ppm STEL for both ECA and MCA. The most recent research (Griffiths, 2000) discovered problems with established sampling methods when used for testing compliance with this limit. It appears that the glass Tenax tube sampling suffers from large losses at low levels possibly due to polymerisation on the first glass wool plug. The research highlighted a need for a modified Tenax tube which performs well at (and below) the new STEL and also for a full assessment of the suitability of Automated Thermal Desorption (ATD) as an alternative analytical technique to solvent desorption/HPLC for the monitoring of cyanoacrylates.

2 EXPERIMENTAL TECHNIQUES

2.1 STANDARD ATMOSPHERES

Dynamic standard atmospheres were used throughout the research, a schematic of the set up used is shown in figure 1.

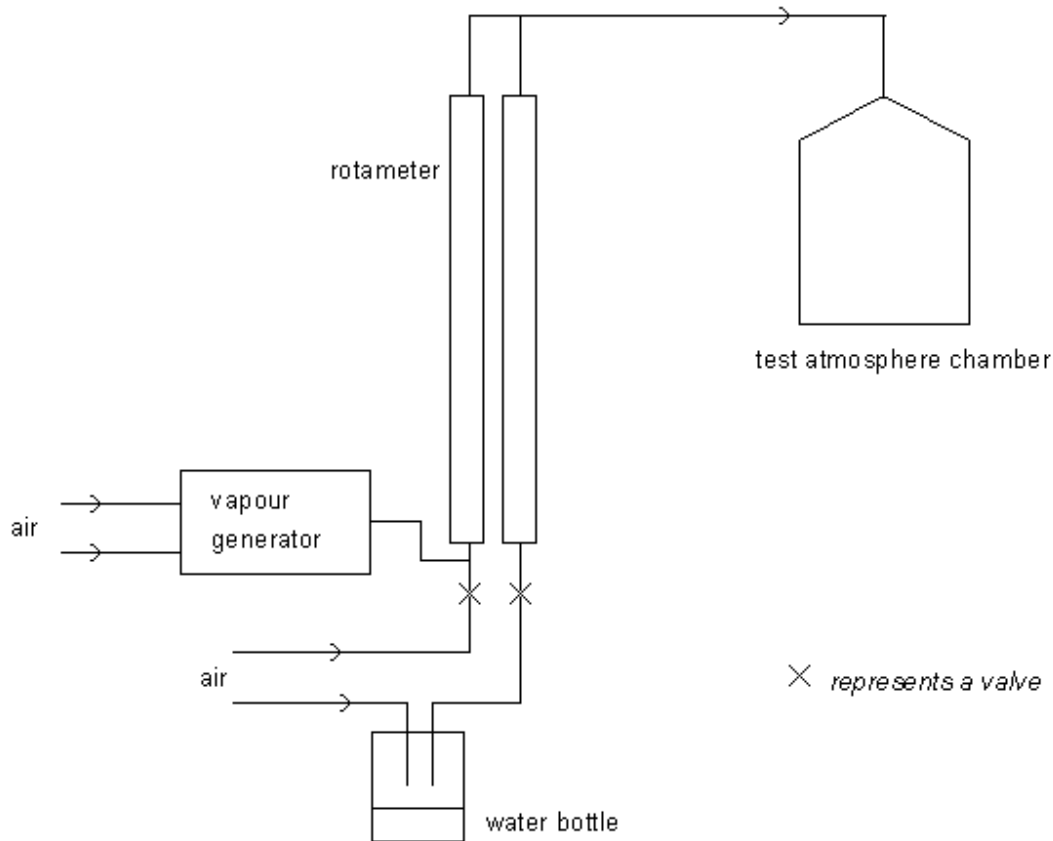


FIGURE 1 - Schematic lay-out of test atmosphere apparatus

Cyanoacrylate vapour was generated by the heating of a permeation source in the oven of the Graseby vapour generator, dry air flowed through the oven at 200 ml/min. Both humidified (using a heated water source) and dry diluent air enabled the humidity in the chamber to be controlled as required. The test chamber had six sampling ports and was double skinned so temperature controlled water could be pumped through to control air temperature inside the sampling chamber. The water contained ethylene glycol to allow sub-zero temperatures required for low temperature work. The concentration of cyanoacrylate was varied by altering the temperature of the oven and/or the number of permeation vials (either 1 or 3) in the vapour generator.

2.2 SAMPLING METHODS

Reference method

Impinger sampling is impractical for personal sampling, however, its value as a reference method has been shown (Keen and Pengelly 1996). Impinger sampling has been used here to enable performance of experimental sampling techniques to be quantified. The volume of solution used throughout the work was 10 ml and sampling flow rate was 500 ml/min.

Pumped Tenax ATD method

Sampling flow rate = 200 ml/min.

Pumped Glass Tenax HPLC methods

Sampling flow rate = 200 ml/min

2.3 SILANISATION OF GLASSWARE

To investigate possible sample adsorption on glassware used for the preparation of stock solutions, a comparison between silanised and unsilanised glassware was made. A total of twelve ECA stock solutions were prepared, six used silanised volumetric flasks and six used unsilanised volumetric flasks. Each stock solution was then analysed by HPLC and a response factor calculated. The response factor is worked out by integrating the area under the peak generated by ECA and dividing it by the concentration of the stock solution. Average response factors were very similar (silanised = 35500 area counts per ppm, unsilanised = 37794). One would expect the response factors for the silanised glassware to be higher, however, due to a lower relative standard deviation (3.6% vs 7.3%) it was decided to use silanised glassware for the preparation of stock solutions.

Silanisation procedure

The glassware is deactivated by rinsing thoroughly with a 5% solution of dichlorodimethylsilane in cyclohexane. The glassware is then rinsed three times in cyclohexane and washed (end capped) with methanol.

3 AUTOMATED THERMAL DESORPTION (ECA ONLY)

3.1 SYSTEM

The system comprised Perkin Elmer Turbomatrix Automated Thermal Desorption (ATD) unit fitted with Tenax TA 80/100 (30 mg) trap coupled to Perkin Elmer Autosystem XL Gas Chromatograph (GC) fitted with HP5 equivalent column (30 m x 0.25 mm ID x 0.25 µm film thickness) and using Turbomass Gold Mass Spectrometer (MS) with chemical ionisation capability. ATD was performed in a two stage desorption process with a transfer of desorbed vapours to the GC by a regulated flow of helium via a transfer line heated at a constant 225 °C. Primary desorption was for 10 min at 250 °C (300 in later work) with vapours being trapped onto a Perkin-Elmer air monitoring cold trap set at -35 °C followed by secondary desorption from the cold trap at 300 °C for 10 minutes (5 in later work). Initially the ATD was set up to give a split of ~ 10% (single split; desorb flow 16.5 ml/min; outlet 8 ml/min) in later work the split ratio was ~ 3% (single split; desorb flow 29.3 ml/min; outlet 30 ml/min). The transfer line to the mass spectrometer was set at 280 °C and the oven temperature was isothermal (200 °C) throughout the 20 minute runtime. The mass spectrometer was set to collect scan and/or (depending upon experiment) selected ion monitoring data (m/z 52, 80, 91, 98).

3.2 STANDARD SOLUTIONS

ECA stock solutions were prepared in: Acetone (+ 0.1% methane sulfonic acid)
Dichloromethane
Dichloromethane (+ 0.2 % phosphoric acid)
Acetonitrile (+ 0.2 % phosphoric acid)

The use of different solvents allowed any potential effects during the tube spiking process to be assessed.

A range of working calibration standards were prepared from the stock solution to give a calibration range corresponding to 0.015 – 1.2 ppm based on a 15 minute sample taken at 200 ml/min when using a 10 µl spike onto the ATD tube.

3.3 EXPERIMENTAL AND DISCUSSION

Tenax ATD tubes were spiked with the working calibration standards so that a calibration line could be derived. The tubes were analysed and a non-linear response was observed in all cases, regardless of the solvent in which they were made up.

To see if there were problems with the spiking process it was decided to attempt to prepare a calibration using standards prepared by loading them direct from the vapour generator for 1, 2, 5, 10, 20 and 30 minutes. The longer the tube loading time, the higher the concentration one would expect. However, the relationship was found not to be linear. For example the 5 minute tube compared to the 2 minute tube gave a response only 17% higher despite a loading time 2.5 times greater and compared to the 10 minute tube the 20 minute tube gave a response 5.5 times greater for only a 2 times increase in the loading time. To check desorption efficiency, a

possible cause for the discrepancy, the 30 minute tube was desorbed a further 2 times and no ECA was observed so the desorption process was considered to be satisfactory.

To check for consistency, replicate analyses were performed: 6 x 5 mins loading direct from vapour generator and 6 x DCM based working standard spiked tubes were prepared and analysed. The relative standard deviation (RSD) for the 5 minute loaded samples was 42% and 74% for the liquid spiked tubes.

To check for any problems with sampling it was decided to introduce an internal standard into the standard atmosphere, toluene is routinely sampled and analysed by ATD using Tenax tubes and so was ideal for checking for any sampling losses/problems. The toluene was added using a separate permeation vial in the vapour generator oven. Several standard atmosphere runs were completed, taking 6 samples per run. The RSD for the toluene was typically around 12% compared to 75-90% for ECA. So the standard atmosphere and sampling technique have been shown to be functioning properly.

Reasons for the unsatisfactory performance of ATD are not clear, it seems possible there are losses during the thermal desorption process and, given the low levels involved these become highly significant. Further work may identify the problem(s), it was decided to concentrate remaining resources on the HPLC and modified glass Tenax tube method.

4 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

4.1 SYSTEM

The HPLC system comprised Waters 600 controller, Waters 996 Diode Array Detector (DAD) and Waters 717plus autosampler. Instrument software used was Waters millennium. The HPLC column was a Waters Spherisorb 5 μ m ODS2 4.6 x 250 mm. The column was kept at a constant 0 °C using a Jones chromatography 7955 heater/chiller system. Injection volume was 50 μ l. Column flow rate was 1 ml/min using a 70/30 0.2 % aqueous phosphoric acid/acetonitrile mobile phase, under these conditions retention times were; ECA 15.5 minutes and MCA 9.1 minutes.

4.2 STANDARD SOLUTIONS

Six ECA stock solutions were prepared in acetonitrile, with 0.2 % phosphoric acid added, using silanised glassware. A further six replicates were prepared using unsilanised glassware, all solutions were within a 50-165 ppm range. Each stock solution was analysed by HPLC and a response factor was calculated. While response factors were comparable, the decision was taken to use the solutions prepared in silanised glassware due to a slightly lower RSD and also due to concerns over possible adsorption effects over prolonged storage.

Two of the silanised stock solutions were selected and six stock dilutions prepared from each to give a range of working standards corresponding to:

0.015 ppm
0.03 ppm (0.1 x OES)
0.1 ppm
0.3 ppm (1 x OES)
0.6 ppm (2 x OES)
1.2 ppm

This is assuming 10 ml in each impinger and a 15 minute sampling time at 500 ml/min.

4.3 EXPERIMENTAL AND DISCUSSION

Good recovery of spiked cyanoacrylate from Tenax tubes has already been demonstrated (Keen & Pengelly, 1996) so it was not felt necessary to repeat these experiments.

4.3.1 Preparation of Tenax sampling tubes

All tubes used were based on a glass SKC Tenax tube (SKC ref 226-35-03) which has a front bed with 100 mg Tenax and a back up bed containing 50 mg Tenax with glass wool plugs before and after the each sorbent bed. Unless otherwise stated all glass tubes were prepared in-house. Figure 2 shows tubes types 3, 8 and the standard 226-35-03 tube upon which they are based.

Tube 1 - Custom built with Teflon wool

A custom built tube supplied by SKC in which the glass wool plugs are replaced by Teflon wool plugs. (SKC lot number 2442).

Tube 2 – Fully silanised

Approximately 10 mm is removed from the front of the tube and all contents then removed. The glass tube is then silanised before being repacked using silanised glass wool in place of the glass wool.

Tube 3 – H₃PO₄ treated

Both ends are snapped off the tube before it is soaked in a 5% phosphoric acid in acetonitrile solution, typically overnight. The tube is then rinsed with acetonitrile and then dried by passing a stream of dry air through the tube for around five minutes.

Tube 4 – Silanised glass wool

The front glass wool plug is removed and replaced with a few strands of silanised wool sufficient to hold the Tenax sorbent in place.

Tube 5 – GF/A plug

The front glass wool plug is removed and replaced with a piece of GF/A filter sufficient to hold the sorbent in place.

Tube 6 – Silanised GF/A plug

The front glass wool plug is removed and replaced with a piece of silanised GF/A filter holding the sorbent in place.

Tube 7 – Steel mesh

The front glass wool plug is replaced with a stainless steel mesh held in place by a v-shaped piece of steel wire.

Tube 8 – Steel mesh/polypropylene o-ring

The front glass wool plug is replaced with a stainless steel mesh held in place by a polypropylene o-ring.

Tube 9- Wholly silanised tube

The ends are snapped off and then the entire tube including contents is silanised.

Tube 10 – Front wool plug removed.

The front glass wool plug is removed, care was required as the sorbent was free to move around and could have been lost.

Tube 11 – H₃PO₄ treated glass wool

The front glass wool plug is replaced with H₃PO₄ treated glass wool (commercially produced).

4.3.2 Standard atmosphere work

All initial work to determine the best tube was carried out at low level, typically around 0.1 x OES (0.03 ppm) as previous work has shown the losses to be more significant at lower levels.

Testing for each tube consisted of at least one 15 minute standard atmosphere run where six samples are taken, three are impinger samples taken for use as the reference method and the remaining three are the tubes under test. In later runs a splitter allowed two samples to be taken per pump for tube sampling, so in these instances six tube samples were taken. After sampling each impinger was made back up to 10ml. For the tubes each sorbent bed was solvent desorbed separately in a silanised 4 ml vial using 2 ml of acetonitrile containing 0.2 % phosphoric acid. Chamber conditions for all these runs were roughly constant at around 20°C and 20 % relative humidity .

4.3.3 Results and discussion

The results of these tests are shown in table 1 and are expressed as a percentage recovery using the impinger as the true result.

Tube type	Concentration range	Number of replicates	Average recovery (%)
1. Custom built Teflon wool plugs	0.03 ppm	N=24 (split over 7 runs)	41
2. Fully silanised	0.03 ppm	N=6 (split over 2 runs)	82
3. H ₃ PO ₄ treated	0.03 ppm	N=15 (split over 4 runs)	89
3. H ₃ PO ₄ treated	0.3 ppm	N=12 (split over 2 runs)	106
4. Silanised glass wool –few strands	0.03 ppm	N=6	76
5. GF/A plug	0.03 ppm	N=3	52
6. Silanised GF/A plug	0.03 ppm	N=3	52
7. Steel mesh	0.03 ppm	N=6 (split over 2 runs)	75
8. Steel mesh/o-ring	0.03 ppm	N=6	87
8. Steel mesh/o-ring	0.3 ppm	N=12 (split over 2 runs)	100
9. Silanised (whole tube)	0.03 ppm	N=3	72
10. Front wool plug removed	0.03 ppm	N=3	103
11. H ₃ PO ₄ treated glass wool plug	0.03 ppm	N=6	71

Looking at the results we can see there are several tubes which give good recoveries (>80%). It was hoped that the custom built tubes with the Teflon wool plugs (tube type 1) would have performed better, as Teflon is an inert material. Likely cause of the poor performance is the large surface area of the wool plug creating sites where moisture can accumulate and thus catalyse the polymerisation of the cyanoacrylate before it can make its way onto the Tenax

sorbent. This concurs with previous research (Griffith, 2000) where it was shown when replacing the glass wool plug with just a few strands of silanised wool, near 100% recoveries could be achieved compared to around 50% for the tube with the original glass wool plug still in place.

Tube type 4 which has a few strands of silanised wool gave an average recovery of 76% which is lower than previous results (Griffith, 2000). This is possibly due to the variability in quantity of replacement silanised glass wool. This was the main drawback with this type of tube; unless the amount of glass wool used is the same each time there is potential for variable recoveries. The preparation of tubes by different people/organisation would only make the chances of this happening even greater.

Tube type 2 which is fully silanised gave good results but was discounted due to it being particularly time consuming to prepare.

During the early stages of the HPLC work it was decided the HPLC data processing conditions would be altered in order to improve the sensitivity of the method. When compared to data obtained using detection at 220nm it was found detection at 212.5 nm improved sensitivity by around 40% and gave a limit of detection of 2.5 ppb, previously 4 ppb. Several sets of data were processed using both wavelengths this showed almost identical results but with the increased sensitivity observed. All subsequent work used 212.5 nm as the detection wavelength.

It was decided that tube types 3 and 8 (H_3PO_4 treated and steel mesh/polypropylene o-ring) would be taken forward for full validation. The decision was based primarily on their excellent recoveries at 0.1 x OES, relative ease of preparation and applicability for other researchers/analysts.

5 METHOD VALIDATION

5.1 VALIDATION CRITERIA

Previous validation work (Keen & Pengelly, 1996) had used BS EN482 as guidance, and it was decided to use the same approach in the validation of the two tubes selected.

Satisfactory performance of a method is based on the relative overall uncertainty, which we shall call a .

$$\text{Relative overall uncertainty, } a = \frac{b - c + 2s}{c} \times 100 \%$$

Where: b = is the mean value of results from repeated measurements using the test method (there must be at least 6)

c = is the true or accepted reference value of concentration (i.e. the mean of impinger results).

s = is the standard deviation of measurements taken by the test method

BS EN 482 requires, for the purposes of measuring for comparison with limit values, that the relative overall uncertainty is $\leq 30 \%$ at $0.5 - 2 \times \text{OES}$ and $\leq 50 \%$ at $0.1 - 0.5 \times \text{OES}$.

5.2 RESULTS AND DISCUSSION

Both types of tubes were validated across a range of temperatures, humidities and concentrations, a summary of the validation results are shown in tables 2 and 3, with full validation data available in the appendices.

The performance of the H_3PO_4 treated tube is slightly worse than its steel mesh/o-ring counterpart, with 4 failures. All but one of these are at the extremes of temperature and humidity. In practice this is not likely to be a particular problem as these conditions are unlikely to be found in the general workplace environment.

The performance of the steel mesh is very good and has passed the validation criteria for all except one experiment. The experiment, measuring an atmosphere of $2 \times \text{OES}$ (0.6 ppm) MCA at high temperature and high humidity, is conducted under conditions which are extremely unlikely to be experienced in a workplace environment. Additionally the use of MCA is far less commonplace than ECA.

NOTE: In cases where the validation criteria have not been fully satisfied, the relative standard deviation for all measurements is still low ($<15 \%$). It may be that the reason for the failure is due to slight problems with the reference method in dealing with sampling in these extremely water laden atmospheres.

The sampling capacity of the tubes was not fully investigated because it was shown that there was no breakthrough at $2 \times \text{OES}$. Furthermore in previous work (Keen & Pengelly, 1996) it

was shown that, using the same sampling time and flow rate, Tenax tubes were able to sample cyanoacrylate atmospheres at 8 ppm without breakthrough occurring.

Table 2. Validation results for H₃PO₄ treated Tenax tubes (type 3)

Experiment	Concentration	Temperature	Relative Humidity	Validation – Pass/Fail
Ethyl cyanoacrylate (ECA)				
1	0.1 x OES	10	10	PASS
2	0.1 x OES	10	60	PASS
3	0.1 x OES	30	40	PASS
4	0.1 x OES	30	10	PASS
5	2 X OES	10	10	PASS
6	2 x OES	30	10	PASS
7	2 x OES	30	60	FAIL
8	2 x OES	10	60	PASS
9	1 x OES	20	10	PASS
Methyl cyanoacrylate (MCA)				
10	0.5 x OES	30	60	FAIL
11	0.5 x OES	10	10	PASS
12	1 x OES	20	35	PASS
13	2 x OES	20	35	PASS
14	2 x OES	10	20	FAIL
15	2 x OES	30	75	FAIL

Table 3. Validation results for steel mesh/o-ring Tenax tubes (type 8)

Experiment	Concentration	Temperature	Relative Humidity	Validation – Pass/Fail
Ethyl cyanoacrylate (ECA)				
16	0.1 x OES	10	10	PASS
17	0.1 x OES	10	60	PASS
18	0.1 x OES	30	50	PASS
19	0.1 x OES	30	10	PASS
20	2 X OES	10	10	PASS
21	2 x OES	30	10	PASS
22	2 x OES	30	60	PASS
23	2 x OES	10	60	PASS
24	1 x OES	20	10	PASS
Methyl cyanoacrylate (MCA)				
25	0.5 x OES	30	65	PASS
26	0.5 x OES	10	10	PASS
27	1 x OES	20	35	PASS
28	2 x OES	20	35	PASS
29	2 x OES	10	20	PASS
30	2 x OES	30	70	FAIL

5.3 SHORT TERM STORAGE TRIALS

Often samples are taken by third parties and then sent to our laboratory for analysis. It was decided a series of short term storage trials should be undertaken to determine whether it should be recommended to desorb immediately after sampling or, if stable, samples could be posted and then desorbed on arrival at the analytical laboratory.

The sampling equipment was set up so 2 tube samples could be taken per sampling pump/point so during each run, 12 samples could be taken. Six samples were desorbed immediately with the remaining six being left in sealed plastic bags at room temperature for five days prior to being desorbed. The concentration level used was around 0.6 ppm (2 X OES) and atmospheric conditions of 20°C and 35% R.H. were used. The experiments were performed on both types of tube and using both ECA and MCA. Results of the experiments are shown in table 4.

Table 4. Short term storage trial results

Tube type	Concentration – desorbed immediately	Concentration – desorbed 5 days later	Percentage lost over short term storage
ECA			
H ₃ PO ₄ treated	0.4520 ppm	0.4334 ppm	4 %
Steel mesh/o-ring	0.7311 ppm	0.6719 ppm	8 %
MCA			
H ₃ PO ₄ treated	0.7274 ppm	0.6830 ppm	6 %
Steel mesh/o-ring	0.8113 ppm	0.7266 ppm	10 %

There some relatively small losses over the 5 day period and so it is recommended that tubes are desorbed as soon as possible. In the event of samples being desorbed after sampling at the laboratory analysts may wish to consider applying a 5% correction factor.

5.4 LIMITS OF DETECTION

Estimated limits of detection (LOD) based on a 15 minute sample taken at 200 ml/min are:

ECA, LOD = 2.5 ppb

MCA, LOD= 3 ppb

6 CONCLUSIONS

Lengthy experimentation with Tenax ATD tubes has shown ATD-GC/MS to be unreliable for sampling/analysis of cyanoacrylates at the low levels required.

Several modified glass Tenax sampling tubes were found to perform well at low levels. Two tubes were selected from these, based on relative ease of modification and ease and reliability of preparation. The tubes selected were based on a standard commercially produced Tenax sampling tube. One tube was treated with H_3PO_4 solution, the other tube substituted the front glass wool plug with a steel mesh held in place by a polypropylene o-ring. The H_3PO_4 treated tube is easier and quicker to prepare in larger quantities.

Both types of tube were fully validated using BS EN 482 as guidance, the steel mesh/o-ring tube performed better in the validation process than its counterpart. It is only when sampling in atmospheres with very high moisture contents that there is a possible problem and it is extremely unlikely these conditions will actually be encountered in a typical workplace environment.

7 REFERENCES

HSL Internal Reports

C Keen and I Pengelly (1996); Measurement of airborne alkyl-2-cyanoacrylates. HSL internal report IR/L/SP/96/08

J R Griffiths (2000); Measurement of alkyl-2-cyanoacrylates at low concentrations. HSL internal report OMS/2000/04

Location of Data

For full information of experiments performed and results produced are in M. Coldwell's "Measurement of Alkyl-2-cyanoacrylates – Further Work" laboratory notebooks 1 and 2.

Hard copies of all chromatograms, results sheets, calibration data are located in office Robens 209.

Electronic copies of all data generated have been made in duplicate.

8 APPENDICES

Table 5. Validation data for H₃PO₄ treated Tenax tubes

Experiment	Average impinger result (ppm)	Average tube result (ppm) ± % RSD	Overall uncertainty
Ethyl cyanoacrylate (ECA)			
1	0.04883	0.04396 ± 12 %	11 %
2	0.03547	0.03505 ± 5 %	8 %
3	0.0474	0.0517 ± 3 %	15 %
4	0.04967	0.05595 ± 3 %	18 %
5	0.5522	0.5655 ± 3 %	9 %
6	0.6572	0.691 ± 3 %	10 %
7	0.5471	0.6858 ± 7 %	42 % f
8	0.3962	0.3773 ± 9 %	12 %
9	0.2489	0.2579 ± 6 %	17 %
Methyl cyanoacrylate (MCA)			
10	0.0817	0.1026 ± 10 %	51 % f
11	0.0728	0.0747 ± 13 %	29 %
12	0.1844	0.2025 ± 6 %	23 %
13	0.4016	0.4469 ± 3 %	18 %
14	0.4112	0.4587 ± 14 %	44 % f
15	0.3957	0.5343 ± 7 %	54 % f

NOTE: For tube result N=6 except for experiments 10 and 11 for which N=5 due to sampling errors. For impinger results N=3.

f = result deemed to have failed validation criteria.

Validation criteria:

0.1 - 0.5 x limit value (i.e 0.03 – 0.15 ppm) overall uncertainty should be ≤ 50 %

0.5 - 2 x limit value (i.e. 0.15 – 0.6 ppm) overall uncertainty should be ≤ 30 %

Table 6. Validation data for steel mesh/o-ring Tenax.

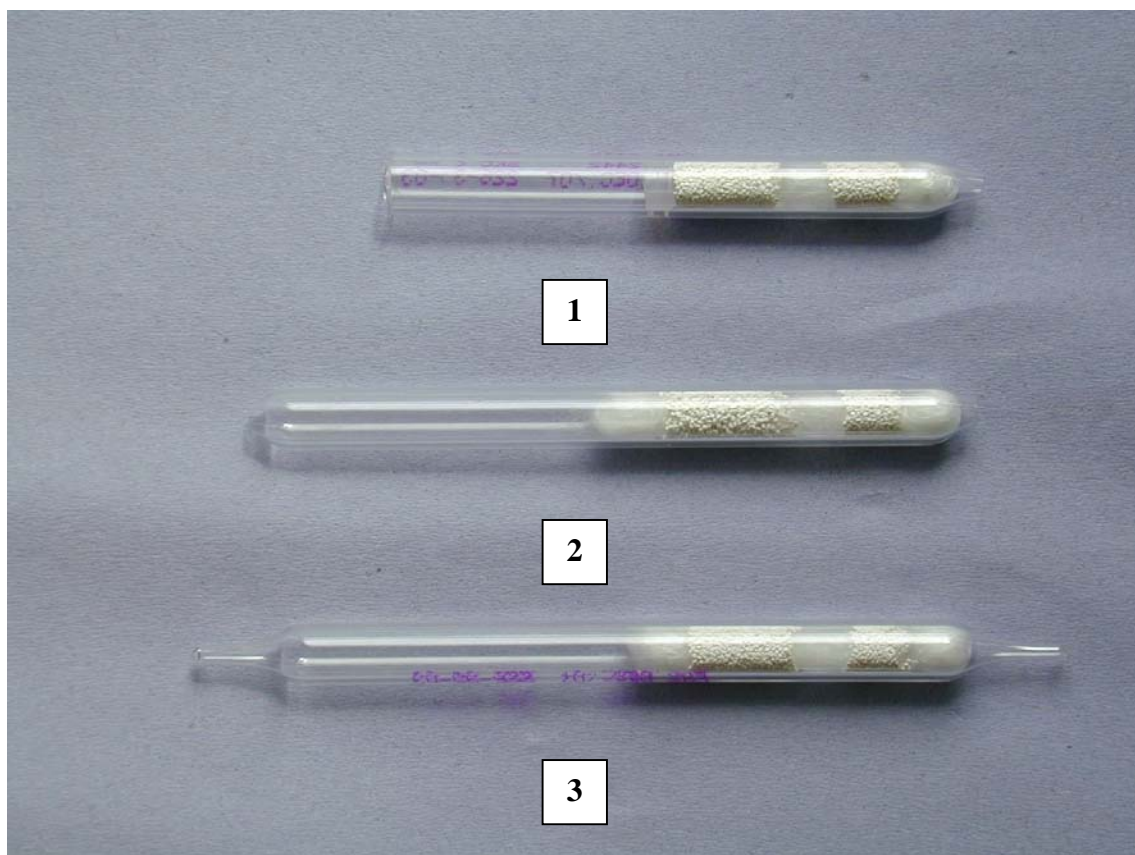
Experiment	Average impinger result (ppm)	Average tube result (ppm) \pm % RSD	Overall uncertainty
Ethyl cyanoacrylate (ECA)			
16	0.04877	0.04365 \pm 13 %	13 %
17	0.0312	0.0273 \pm 14 %	11 %
18	0.0534	0.0518 \pm 3 %	2 %
19	0.0484	0.05513 \pm 4 %	22 %
20	0.587	0.5997 \pm 1 %	4 %
21	0.6384	0.7169 \pm 3 %	10 %
22	0.5645	0.6686 \pm 3 %	26 %
23	0.3562	0.3143 \pm 9 %	4 %
24	0.2265	0.2418 \pm 7 %	23 %
Methyl cyanoacrylate (MCA)			
25	0.0865	0.1139 \pm 2 %	37 %
26	0.0775	0.0811 \pm 18 %	43 %
27	0.2746	0.3082 \pm 1 %	14 %
28	0.3802	0.4041 \pm 2 %	11 %
29	0.4347	0.4974 \pm 6 %	28 %
30	0.4029	0.5450 \pm 5 %	49 % f

NOTE: For tube result N=6 except for experiments 20 where N=4, experiment 24 where N=5 and for experiment 27 where N=4 due to sampling errors. For impinger results N=3. f = result deemed to have failed validation criteria.

Validation criteria:

0.1 - 0.5 x limit value (i.e 0.03 – 0.15 ppm) overall uncertainty should be \leq 50 %
 0.5 - 2 x limit value (i.e. 0.15 – 0.6 ppm) overall uncertainty should be \leq 30 %.

Figure 2. Tenax sampling tubes.



- 1 = Tube type 8 – Polypropylene o-ring/steel mesh Tenax
- 2 = Tube type 3 – Phosphoric acid treated Tenax
- 3 = Standard Tenax tube SKC part number 226-35-03

Measurement of alkyl 2-cyanoacrylates at low concentrations

Further work

This report describes research into improved cyanoacrylate sampling methods. The research was an assessment of Automated Thermal Desorption (ATD) as an alternative sampling/analytical technique for the measurement of airborne cyanoacrylate and the development of modified Tenax sampling tubes.

HSE introduced the 0.3 ppm Short-term exposure limit (STEL) in 2000 for both ethyl-2-cyanoacrylate (ECA) and methyl-2-cyanoacrylate (MCA). These limits were transposed into Workplace Exposure Limits (WELs) in 2005, with revised compliance criteria. HSE investigated the ability of existing sampling methods to test compliance with the limit and found significant errors. Sampling losses are apparently due to polymerisation on the glass wool plug of the Tenax tube used for sampling.

Eleven types of modified Tenax tube were prepared and evaluated at 0.03 ppm using a dynamic standard atmosphere. Analysis was by High Performance Liquid Chromatography (HPLC) with Ultra-Violet (UV) detection. Two tubes were found to compare well with the impinger based reference method. One tube replaces the front wool plug with a steel mesh and polypropylene o-ring to hold the sorbent in place. The other tube is treated with a phosphoric acid solution. Both tubes were subjected to a thorough laboratory validation, using BS EN482 as guidance. The steel mesh/o-ring tube performed slightly better than its counterpart when sampling MCA atmospheres and hence is the preferred choice. This tube is capable of providing reliable and sensitive measurement of cyanoacrylate atmospheres across a range of concentration, temperature and humidity.

This report and the work it describes were funded by the Health and Safety Executive (HSE). Its contents, including any opinions and/or conclusions expressed, are those of the author alone and do not necessarily reflect HSE policy.