Health and Safety Executive

Field validation of improved sampling methods for airborne cyanoacrylates

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

RR646
Research Report

HSE

Health and Safety Executive

Field validation of improved sampling methods for airborne cyanoacrylates

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This report describes a field validation exercise undertaken to assess improved cyanoacrylate sampling methods. HSL has developed revised sampling methods for ethyl-2-cyanoacrylate (ECA) and methyl-2-cyanoacrylate (MCA) following the introduction of the 0.3 ppm Short-term exposure limit (STEL) in 2000, see report RR645. These limits were transposed into Workplace Exposure Limits (WELs) in 2005, with revised compliance criteria.

A three-site, four visit field validation exercise has been carried out. The sites visited were a Police scene-of-crime laboratory, an automotive loudspeaker manufacturer and a producer of adhesives which was visited on two occasions. Static sampling was performed using an impinger based reference method together with the two newly developed tubes. The tubes are based on a commercially available Tenax tube, which has 100 mg sorbent bed and 50 mg back-up bed. 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 performed well and the results were generally in good agreement with the reference method over a representative range of concentrations. Both tubes were found to be suitably robust for fieldwork. It is recommended the tube with steel mesh be used for all measurement of airborne cyanoacrylate concentrations due to better performance in laboratory validation tests.

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.

HSE Books

First published 2008

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EXECUTIVE SUMMARY

Main Findings

Field validation of new cyanoacrylate sampling tubes has been carried out.

Four sites have been visited and airborne cyanoacrylate exposure monitored using a reference sampling method and the newly developed tubes side-by-side. Good correlation between the reference method and the new tubes has been achieved.

The tube which uses a steel mesh has been found to perform better than its counterpart in previous laboratory validation and therefore, is the preferred choice.

Recommendations

It is recommended that measurements of airborne cyanoacrylate exposure should be carried out using the new steel mesh sampling tube.

Attempts should be made to establish commercial production of the new sampling tube.

1 INTRODUCTION

In 2000 HSE introduced an exposure limit of 0.3 ppm (STEL) for ethyl-2-cyanoacrylate (ECA) and methyl-2-cyanoacrylate (MCA). To test compliance with this limit research was carried out on existing sampling methods (Griffiths, 2000). It was found that some sampling tubes were underestimating exposure by as much as 50% at this level. This was thought to be due to the cyanoacrylate polymerising on the glass wool plug at the sampling end of the tube.

In follow-on research HSL has developed two new sampling tubes (Coldwell, 2003), which in laboratory tests perform comparably to an established reference method. Both tubes are based on a common Tenax sampling tube (SKC part number 226-35-03), one tube has the first glass wool plug removed and replaced with a steel mesh held in place by a polypropylene o-ring. The other tube is treated with a phosphoric acid solution. The reference method uses an impinger containing a 5% phosphoric acid in acetonitrile solution. Further details of sampling methods are given in section 2.

Before the method could be officially approved it was decided that a field validation study should be carried out to compare the performance of the new tubes with the reference method in the actual workplace environment.

2 SAMPLING STRATEGY

To allow a proper evaluation of the performance of the new sampling tubes to be made they would have to be used side-by-side with the impinger reference method. The impinger method is impractical for use as a personal sampler, with particular concerns over the glass construction and the use of solvent. It was decided that static sampling would be the to key to the validation exercise as all three methods could be directly compared with minimal disruption to workers.

Static sampling positions were chosen to reflect workplace exposure patterns. However, to assess the performance of the method at higher concentrations there were a small number of samples intentionally located in areas where cyanoacrylate concentrations would be high. These results should not be taken as representative of typical exposures.

Personal sampling was conducted using a single pump with a dual flow adjuster so the breathing zone of the subject could be monitored using both tubes, thus gaining extra data on how the tubes compare against each other.

Flow rates were 200 ± 10 ml/min for the tubes and 500 ± 10 ml/min for impingers. Flow rates were checked before and after sampling.

3 SITE SELECTION

A large-scale survey of cyanoacrylate usage and exposure was carried out in 1997; this scoped many different industries and was used as the basis for site selection.

For this survey it was recognised that it would not be possible to include all industries where cyanoacrylate exposure could occur, so it was decided that a representative cross-section of cyanoacrylate users should be taken.

Sites selected were;

- A manufacturer of cyanoacrylate adhesives, which also included repackaging and laboratory testing operations, this site, was visited twice.
- A large manufacturer of automotive speakers
- A Police fingerprint laboratory.

Attempts were made to visit manufacturers of lampshades and UPVC windows but considerable difficulties were encountered arranging these and they were not undertaken.

4 SITE DESCRIPTIONS

4.1 SITE 1

Site 1 was a major manufacturer of cyanoacrylate adhesives. The site also had an on-site packaging plant and laboratory facilities. Cyanoacrylate exposure was measured for all major tasks in all three areas.

The packaging plant allowed bulk adhesives to be repackaged into smaller retail ready containers – tubes, bottles etc. Exposure monitoring was carried out at this site on two occasions, to assess exposures before and after the commissioning of a new packaging plant.

4.2 SITE 2

Site 2 was the fingerprint laboratory of a Police headquarters. The main equipment used for the operations was a Mason Vactron MVC5000 fingerprint cabinet, which is fully automated.

4.3 SITE 3

Site 3 was a large producer of automotive speakers. The manufacturing operations included a number of different production lines, all of which may be using cyanoacrylate adhesives depending on the particular components being assembled. The adhesive was dispensed by an automated system operating under pressure. Typically, once a shift, vessels are recharged with adhesive, and this is carried out by a nominated glue technician. On the day of the visit only one of the main production lines was using a cyanoacrylate based adhesive.

5 RESULTS AND DISCUSSION

Static sampling results are given in this section. Full personal sampling results are given in the appendices.

Table 1. Static sampling results for site 1 visit 1.

SAMPLE		ECA CONC
		ppm
Static 1	Imp 1	ND (<0.02)
	Steel mesh tube 5a	0.04
	Acid treated tube 5b	0.04
Static 2	Imp 2	0.10
	Steel mesh tube 10a	0.21
	Acid treated tube 10b	0.24
Static 3	Imp 3	0.02
	Steel mesh tube 7a	0.19
	Acid treated tube 7b	0.19
Static 4	Imp 4	0.23
	Steel mesh tube 13a	0.19
	Acid treated tube 13b	0.30
Static 5	Imp 5	1.14
	Steel mesh tube 15a	1.02
	Acid treated tube 15b	0.74
Static 6	Imp 6	1.85
	Steel mesh tube 16a	1.95
	Acid treated tube 16b	2.64

There is good comparison between methods for result sets 1 and 4 to 6. There is no obvious reason for the discrepancy in result sets 2 and 3, flow rates were checked before and after sampling and no problems reported.

Table 2. Static sampling results for site 1 visit 2.

SAMPLE		ECA CONC
		ppm
Static 1	Imp 1	0.48
	Steel mesh tube 3a	0.55
	Acid treated tube 3b	0.64
Static 2	Imp 2	0.17
	Steel mesh tube 4a	0.20
	Acid treated tube 4b	0.20
Static 3	Imp 3	0.95
	Steel mesh tube 8a	1.03
	Acid treated tube 8b	1.08
Static 4	Imp 4	0.42
	Steel mesh tube 11a	0.34
	Acid treated tube 11b	0.35
Static 5	Imp 5	0.20
	Steel mesh tube 12a	0.16
	Acid treated tube 12b	0.18
Static 6	Imp 6	0.18
	Steel mesh tube 15a	0.26
	Acid treated tube 15b	0.24
Static 7	Imp 7	0.17
	Steel mesh tube 16a	Sample lost
	Acid treated tube 16b	0.20
Static 8	Imp 8	0.16
	Steel mesh tube 17a	0.18
	Acid treated tube 17b	Sample lost
Static 9	Imp 9	0.28
	Steel mesh tube 18a	0.28
	Acid treated tube 18b	0.29
Static 10	Imp 10	0.21
	Steel mesh tube 19a	0.20
	Acid treated tube 19b	0.21
Static 11	Imp 11	0.17
	Steel mesh tube 20a	0.17
	Acid treated tube 20b	0.18
Static 12	Imp 12	0.18
	Steel mesh tube 21a	0.18
	Acid treated tube 21b	0.16

There is excellent correlation between the tube results and the reference impinger method with no discrepancies of any significance. It is also worth noting that a good number of these results are at concentrations of at least 50% of the limit value. Fig 1 shows a graphical comparison of these results.

Table 3. Static sampling results for site 2.

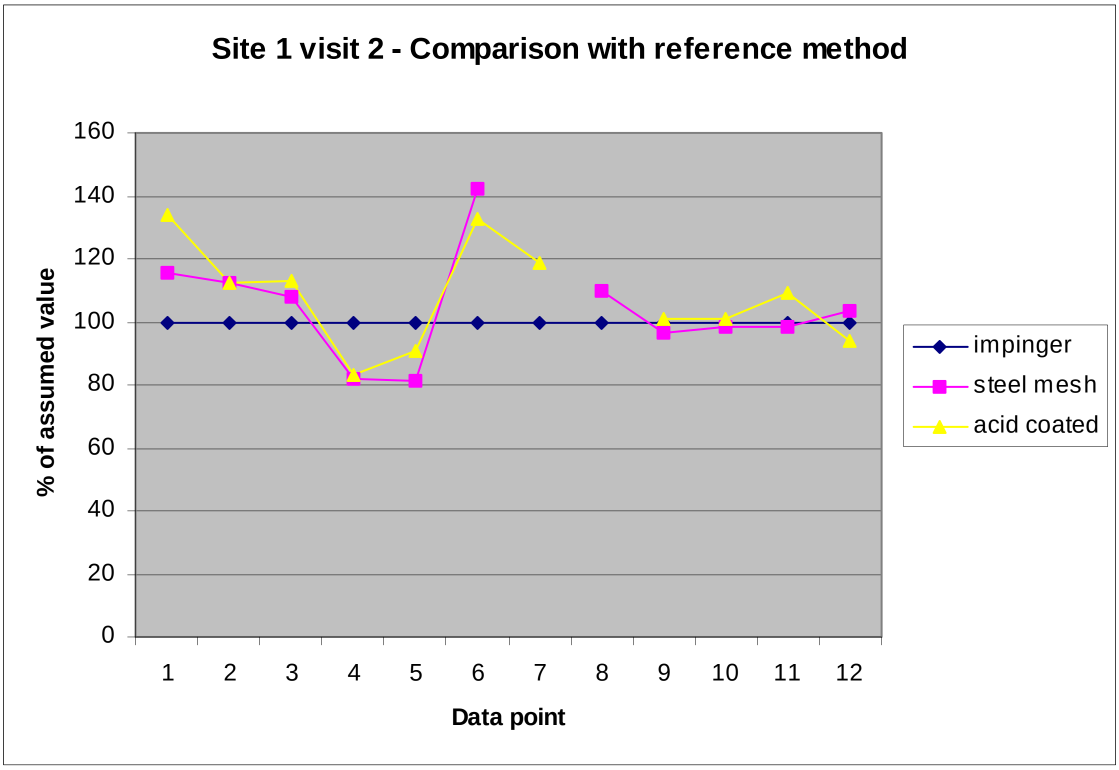
SAMPLE		ECA CONC
		ppm
Static 1	Imp 2	0.02
	Steel mesh tube 3a	0.02
	Acid treated tube 3b	0.02
Static 2	Imp 3	0.05
	Steel mesh tube 7a	0.02
	Acid treated tube 7b	ND (<0.01)
Static 3	Imp 4	0.03
	Steel mesh tube 8a	0.03
	Acid treated tube 8b	0.04

Table 4. Static sampling results for site 3.

SAMPLE		ECA CONC
		ppm
Static 1	Imp 1	ND (<0.02)
	Steel mesh tube 10a	ND (<0.02)
	Acid treated tube 10b	ND (<0.02)
Static 2	Imp 2	0.02
	Steel mesh tube 7a	0.02
	Acid treated tube 7b	0.02
Static 3	Imp 3	ND (<0.02)
	Steel mesh tube 13a	ND (<0.02)
	Acid treated tube 13b	ND (<0.02)
Static 4	Imp 4	ND (<0.02)
	Steel mesh tube 12a	ND (<0.02)
	Acid treated tube 12b	ND (<0.02)
Static 5	Imp 5	0.04
	Steel mesh tube 8a	0.06
	Acid treated tube 8b	0.04

The results for sites 2 and 3 show good agreement between test and references methods when measuring workplace atmospheres with zero or low cyanoacrylate concentrations.

Figure 1. Comparison of static sampling results for site 1 visit 2.



Summary

The static sampling exercise has shown good agreement between test and references methods when measuring workplace cyanoacrylate atmospheres over a representative concentration range i.e. zero to the limit value.

The personal sampling results show that there is good agreement between both tube types over a similar concentration range to that mentioned above. There are a small number of discrepancies in the results with no obvious explanation. It is thought, given the comparable performance during laboratory validation (Coldwell, 2003) the losses may be attributed to general sampling error.

The tube sampling is easier to perform than the impinger method and is much less obtrusive to the operators wearing it. Furthermore there are no issues over restricted movement; sample can be lost when using the impinger if an operator leans over. The tubes are used with holders, which cover the tube, so there are no risks from cuts from the open end of the tube. There are definite potential risks when using an impinger with the use of solvent and its glass construction.

Both tubes were found to be robust enough to be used in the field without compromising sampling.
The steel-mesh has been sent out to end-users and sent back through the mail, arriving intact.

Preparation of both tubes is straightforward, with the steel mesh tube being slightly more labour intensive, it is hoped this can be addressed by exploring commercial production options for this tube.

6 CONCLUSIONS

The results obtained from this field trial show that the new sampling tubes perform comparably with the reference impinger method over a concentration range necessary for testing compliance with the limit value.

Both tubes have been found to be suitably robust for field sampling. It is recommended the steel mesh with o-ring tube be used preferentially as it performed better in laboratory validation tests (Coldwell, 2003). Additionally, there are concerns over the effect of the phosphoric acid on the Tenax sorbent and stability of these tubes over time. Preparation of the preferred steel mesh tube is slightly more labour intensive than the acid treated one and therefore, discussions should be held with the tube manufacturers to ascertain if commercial production and supply can be secured.

HSL recommends that all assessments of cyanoacrylate exposure be carried out using the new sampling tube.

7 REFERENCES

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

M R Coldwell (2003); Measurement of alkyl-2-cyanoacrylates at low concentrations – further work. HSL internal report OMS/2003/23.

8 APPENDICES

8.1 METHODOLOGY

8.1.1 Reference sampling method

Impinger containing 10 ml acetonitrile with 0.2% phosphoric acid added. Sampling flow rate = 500 ml/min, sampling time = 15 minutes. Volume made back up to 10 ml after sampling, ready for analysis.

8.1.2 Test sampling methods

Modified sampling tubes (based on SKC tenax tube 226-35-03). Sampling flow rate = 200 ml/min, sampling time = 15 minutes. Each sorbent bed desorbed in 2 ml acetonitrile (with 0.2 % phosphoric acid) ready for analysis.

8.1.3 Analytical method

HPLC-UV equipment used comprised; Waters 600 controller, Water 996 Diode Array Detector (DAD) and Waters 717plus autosampler. Column – Waters Spherisorb 5µm ODS2 4.6 x 250 mm. The column was kept at a constant 0^{o}C by a Jones 7955 heater/chiller system. Injection volume was 50 µl. Column flow was 1 ml/minute using a 70/30 0.2% aqueous phosphoric acid/acetonitrile mobile phase, under these conditions the retention time for ECA was 15.5 minutes. Processing wavelength used was 212.5 nm.

8.2 PERSONAL SAMPLING RESULTS FOR SITE 1

Table 5. Visit 1

SAMPLE		ECA CONC
		ppm
1	Steel mesh 1a Acid treated 1b	0.13 0.14
2	Steel mesh 2a Acid treated 2b	0.01 0.09
3	Steel mesh 3a Acid treated 3b	0.22 0.01
4	Steel mesh 4a Acid treated 4b	0.17 0.19
5	Steel mesh 6a Acid treated 6b	0.12 0.11
6	Steel mesh 8a Acid treated 8b	0.43 0.59
7	Steel mesh 9a Acid treated 9b	0.11 0.13
8	Steel mesh 11a Acid treated 11b	0.19 0.18
9	Steel mesh 12a Acid treated 12b	0.04 0.05
10	Steel mesh 14a Acid treated 14b	0.25 0.26

Table 6. Visit 2

SAMPLE		ECA CONC
		ppm
1	Steel mesh 1a Acid treated 1b	0.06 0.01
2	Steel mesh 2a Acid treated 2b	0.05 0.05
3	Steel mesh 5a Acid treated 5b	0.06 0.07
4	Steel mesh 6a Acid treated 6b	0.06 0.07
5	Steel mesh 7a Acid treated 7b	0.17 0.17
6	Steel mesh 9a Acid treated 9b	0.68 0.01
7	Steel mesh 10a Acid treated 10b	0.17 0.17
8	Steel mesh 13a Acid treated 13b	0.22 0.24
9	Steel mesh 14a Acid treated 14b	0.20 0.21

8.3 PERSONAL SAMPLING RESULTS FOR SITE 2

Table 7. Tube only sampling results.

SAMPLE		ECA CONC
		ppm
1	Steel mesh 1a Acid treated 1b	0.02 0.17
2	Steel mesh 2a Acid treated 2b	0.01 0.01
3	Steel mesh 4a Acid treated 4b	6.44 7.47
4	Steel mesh 5a Acid treated 5b	ND (<0.01) ND (<0.01)
5	Steel mesh 6a Acid treated 6b	ND (<0.01) ND (<0.01)

Note that sample set 3 was not a personal sample – the tubes were used to sample the atmosphere inside the cabinet whilst running as a measure of how the tubes would perform in extreme conditions.

8.4 PERSONAL SAMPLING RESULTS FOR SITE 3

Table 8. Tube only sampling results.

SAMPLE		ECA CONC
		ppm
1	Steel mesh 1a Acid treated 1b	0.08 0.07
2	Steel mesh 2a Acid treated 2b	0.06 0.09
3	Steel mesh 4a Acid treated 4b	ND (<0.01) ND (<0.01)
4	Steel mesh 5a Acid treated 5b	ND (<0.01) ND (<0.01)
5	Steel mesh 6a Acid treated 6b	0.43 0.43
6	Steel mesh 9a Acid treated 9b	0.04 0.04
7	Steel mesh 11a Acid treated 11b	0.04 0.04
8	Steel mesh 14a Acid treated 14b	0.61 0.58
9	Steel mesh 15a Acid treated 15b	0.09 ND (<0.01)
10	Steel mesh 16a Acid treated 16b	0.02 0.02

Published by the Health and Safety Executive 09/08

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