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SAMPLING OF SOLID SURFACES AFTER AN ALLEGED USE OF CHEMICAL WARFARE AGENTS

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8) ABSTRACT
In this report different procedures for sampling of solid surfaces after a suspected attack with chemical warfare agent have been tested. Q-tips wetted with an organic solvent as sampling media, give the highest overall recovery rates for the compounds tested. Q-tips are easy to use in the field. Of the extraction solvents tested, dichloromethane was found to be best suited. The chances of positive identification will be greatly enhanced if the droplets or marks of droplets are visible on the surfaces at the time of sampling.

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CONTENTS

SAMPLING OF SOLID SURFACES AFTER AN ALLEGED USE OF CHEMICAL WARFARE AGENTS

1 INTRODUCTION

After a suspected attack with chemical warfare agents wiping of solid surfaces, such as buildings, vehicles, etc may be used to collect samples for verification purposes. The aim of the experiments described in this report was to develop a uniform procedure for sampling solid surfaces. The experiments were also meant to form the basis for the selection of sampling media and methods for sample preparation. The experiments were based on Recommended Operation Procedures (1). The recovery rate of different chemical agents tested with the different procedures was also of interest.

2 EXPERIMENTAL

2.1 Chemicals

Mustard gas (HD), CAS no 505-60-2, synthesized by FFI
Sarin (GB), CAS no 107-44-8, synthesized by FFI
Diisopropylmethylphosphonate (DIPMP), CAS no 1445-75-6, synthesized by FFI
Acetone, CAS no 67-64-1,ultra resi-analyzed from J T Baker
Acetonitrile, CAS no 75-05-8, HPLC-grade from Rathburn
2-propanol, CAS no 67-63-0, uvasol from Merck
Ethyl acetate (EtAc), CAS no 141-78-6, supraSolv from Merck
Dichloromethane (CH_2Cl_2), CAS no 75-09-2, ultra pure from J T Baker analyzed
Dodecane (C_{12}), CAS no112-40-3, from Koch-Light

2.2 Instrumentation

A MD 800 Fisons quadrupole mass spectrometer (MS) in election ionisation (EI) mode connected to a Fisons HRGC 8060 gas chromatograph (GC) and an AS 800 autosampler were used in all experiments. A sample volume of 1 µl was injected splitless for 1 minute. The GC column used was a DB-5MS (30 m x 0.25 mm) and helium was used as carrier gas with flow rate 1 ml/min. The injector temperature was set to 250 °C, the transfer line to 260 °C and the ion source to 190 °C. The electron energy was set to 70 eV and the filament current was 0.15 mA for the ion source. The oven temperature program was 40 °C (1 min) - 10 °C/min - 280 °C (0 min). The ion source was scanned from 35 – 400 u with scan speed 0.5 sec/scan.

2.3 Sample preparation

Four different sampling media were tested in this report. These were Q-tips, pieces of cotton cloth (10 cm^2), felt (diameter 1.5 cm) and filter paper (diameter 1.5 cm).

Two different solid surfaces were used in the experiments. A painted metal plate with combined layers of epoxy (80 µm), polyurethane (80 µm) and alkyd paint (40 µm) was used to simulate a military vehicle and a crude concrete plate to simulated buildings.

Three different nonpolar organic solvents and one polar organic solvent were tested as wiping solvents in these experiments (1). The solvents were acetone, 2-propanol, ethyl acetate and dichloromethane.

The preparation of the wipe samples was done both with dry and wet sampling media. The wetting agents were the organic solvents mentioned above. Disposable pincers were used to hold the felt and filter paper while preparing the wipe samples. An artery clamp was used for the cotton cloth.

The extraction of the test agents from the sampling media was done in a closed 10 ml test tube as described below. The test tube was sonicated for 5 minutes and the supernatant decanted to an autosampler vial.

Three parallels and one blank were analyzed for each experiment. The quantification was done with an internal standard (C_{12}) by gas chromatography – mass spectrometry (GC-MS) analyzes. Evaluation of possible outliers in the results was done with Deans and Dixons method (2).

2.3.1 Direct extraction

1 µl of HD, GB or DIPMP was applied directly onto dry or ethyl acetate wetted sampling media. The samples were then put into a closed bottle, some empty and some with 1 ml of different organic solvent. The solvents used were acetone, 2-propanol, dichloromethane or ethyl acetate. The extraction was carried out with an ultrasonic bath both after 1 hour and 24 hours storage at room temperature. The purpose of the experiments was to find the most efficient solvent for extracting these test agents and to see if the storage of the samples with or without solvent had any noticeable effects of the recovery rate of the agents. Also the effect of wet sampling media were of interest.

2.3.2 Painted metal plate

1 µl HD, GB or DIPMP was directly applied onto the painted metal plate. The painted metal surface was than wiped off with dry or wetted sampling media after 5 minutes, 6 hours or 24 hours. The solvent used for wetting the sampling media before wiping was 2-propanol, acetone, ethyl acetate or dichloromethane. Dichloromethane or ethyl acetate was used as extraction solvents and the actual extractions were done as described in Chapter 2.3.1.

2.3.3 Crude concrete plate

1 µl of HD, DIPMP or GB was applied directly onto crude concrete and wiped off with wetted sampling media after 5 minutes or 6 hours. Q-tip and cotton cloth was used as sampling media and ethyl acetate as wetting solvent for these experiments. Dichloromethane or ethyl acetate was used as extraction solvents and the actual extractions were done as described in Chapter 2.3.1.

2.3.4 Storage of ethyl acetate in prototype sampling case

The Norwegian Defence NBC School (FABCS) and Norwegian Defence Research Establishment (FFI) has developed a prototype chemical sampling kit for use in verification of alleged use of chemical warfare agents (3)(4). This kit includes all the necessary equipment for collecting different kinds of samples. To see if ethyl acetate got contaminated after storage for a period of time, 10 ml of the solvent was stored in two different test tubes. Kimax glass tubes with teflon-faced rubber lined caps and Venoject glass tubes with rubber caps were tested. The tubes were stored at room temperature for five months prior to GC-MS analyzes.

3 RESULTS AND DISCUSSION

3.1 Sampling of surfaces contaminated with HD

The purpose of these experiments was to find the most suitable extraction solvent and the best sampling media. Acetone, ethyl acetate, 2-propanol and dichloromethane were tested as extraction solvents. Q- tip was compared with cotton cloth, felt and filter paper as sampling media. The extraction solvents were first examined. This was done by applying HD directly onto dry Q- tips and storing them for 1 hour at room

temperature in closed empty vials before extraction with 1 ml organic solvent. The results are given in Table 3.1.

	2-propanol	Acetone	Ethyl acetate	Dichloromethane
Mean (µg)	258 ± 36	317 ± 11	396 ± 52	458 ± 112
Recovery rate (%)	20	25	31	36

Table 3.1 Mean ± standard deviation and recovery rate of HD applied directly onto dry Q- tips and extracted with different solvents

The results given in Table 3.1 show that dichloromethane as the extraction solvent gives the highest recovery rate for HD, but also the highest standard deviation.

As recovery rate did not reach 50 % for any of the solvent tested, sonaication for 15 minutes instead of 5 minutes was tried. This gave an even lower recovery rate.

For storage and transportation it is best to have a solvents with a relatively high boiling point. The boiling points are for ethyl acetate 77 °C, for acetone 57 °C, for 2-propanol 83°C and for dichloromethane 40 °C. Taking the differences in boiling points and the results from the first experiments into consideration it was decided to use dichloromethane and ethyl acetate in future experiments, preferably ethyl acetate.

To collect the best wipe sample of contaminated surfaces it is important to have easy to use sampling media that are easy to include in the prototype sampling kit (3)(4). Q-tips, felt and filter paper spiked directly with HD were evaluated in the next experiment. The sampling media were stored for 1 hour at room temperature before extraction with ethyl acetate or dichloromethane. The results are given in Figure 3.1.

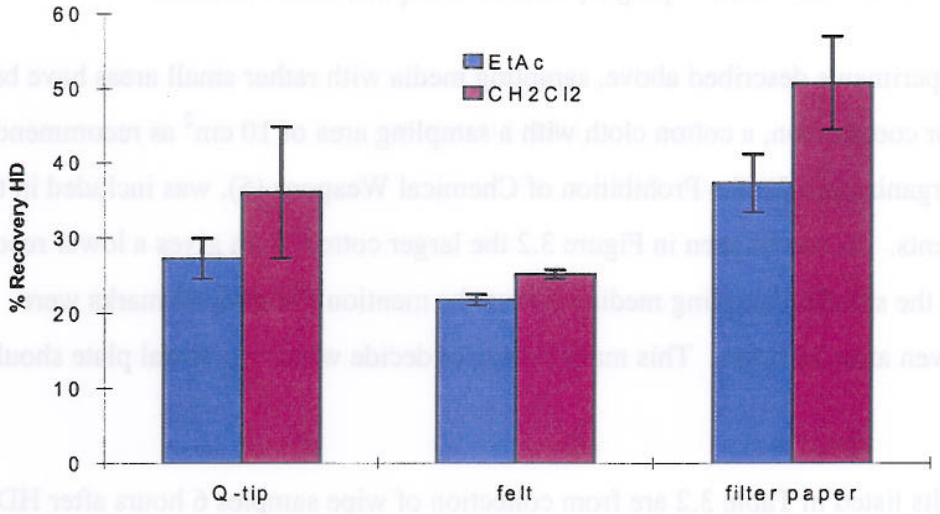

Figure 3.1 The recovery rate of HD applied directly onto dry Q-tip, felt and filter paper and extracted with ethyl acetate or dichloromethane

The results given in Figure 3.1 show that filter paper as sampling medium and dichloromethane as extraction solvent gives the highest recovery rate for HD.

To simulate collection of a wipe sample on-site, several droplets of HD were applied onto a painted metal plate. After a given period of time the surface was wiped with different sampling media both dry and wetted with ethyl acetate. The samples were then stored for 1 hour at room temperature before extraction with ethyl acetate.

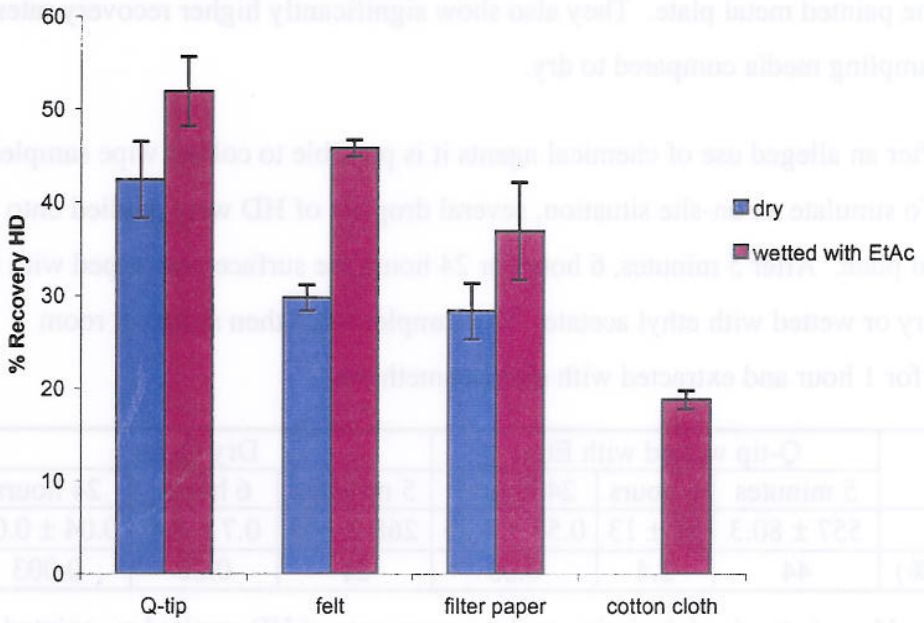

Figure 3.2 The recovery rate of HD applied onto a painted metal plate and wiped after 5 minutes with different sampling media

The results given in Figure 3.2 show that ethyl acetate wetted Q-tips have the highest recovery rate for HD when wiping a painted metal plate after 5 minutes.

In the experiments described above, sampling media with rather small areas have been used. For comparison, a cotton cloth with a sampling area of 10 cm^2 as recommended by the Organization for the Prohibition of Chemical Weapons (5), was included in the experiments. As can be seen in Figure 3.2 the larger cotton cloth gives a lower recovery rate then the smaller sampling media. It must be mention that droplet marks were visible even after 24 hours. This made it easy to decide where the metal plate should be wiped.

The results listed in Table 3.2 are from collection of wipe samples 6 hours after HD was applied onto the painted metal plate. The sampling media used were dry Q-tips and ethyl acetate wetted Q-tips, felt, filter paper and cotton cloth. The extraction was done with ethyl acetate after storing the samples for 1 hour at room temperature.

	Dry	Wetted with EtAc			
	Q-tip	Q- tip	Felt	Filter paper	Cotton cloth
Mean (µg)	1 ± 0.4	67 ± 17	21 ± 3.1	41 ± 3.8	33 ± 4
Recovery (%)	0.1	5.3	1.6	3.2	2.6

Table 3.2 *Mean ± standard deviation and recovery rate of HD applied onto painted metal plate and wiped after 6 hours with different sampling media*

The results in Table 3.2 show that the recovery rates of HD are less than 6 % after 6 hours on the painted metal plate. They also show significantly higher recovery rates for wetted sampling media compared to dry.

How soon after an alleged use of chemical agents it is possible to collect wipe samples may vary. To simulate an on-site situation, several droplets of HD were applied onto a painted metal plate. After 5 minutes, 6 hours or 24 hours the surface was wiped with Q-tips, either dry or wetted with ethyl acetate. The samples were then stored at room temperature for 1 hour and extracted with dichloromethane.

	Q-tip wetted with EtAc			Dry Q-tip		
	5 minutes	6 hours	24 hours*	5 minutes	6 hours	24 hours
Mean (µg)	557 ± 80.3	31 ± 13	0.57 ± 0.25	268 ± 145	0.7 ± 0.4	0.04 ± 0.03
Recovery (%)	44	2.4	0.05	21	0.06	0.003

Table 3.3 *Mean± standard deviation and recovery rate of HD applied on painted metal plate and wiped after 5 minutes, 6 hours and 24 hours with dry and EtAc wetted Q-tips and extracted with dichlorometane*
**) Q-tip wetted with CH_2Cl_2*

The results given in Table 3.3 show that the recovery rate of HD after 6 hours and 24 hours are low. The results also show higher recovery rate for wetted sampling media compared to dry as observed in earlier experiments.

Experiments with acetone, 2-propanol or dichloromethane as wetting solvents have also been carried out but gave approximately the same recovery rates as for ethyl acetate.

It was interesting to see if transportation time and storage conditions had any effect on the recovery rates of HD, with or without prior addition of extraction solvent to the sampling media. HD was applied onto Q-tips, felt and filter paper that were previously wetted with ethyl acetate. The samples were stored for 1 hour or 24 hours at room temperature in empty glass tubes before extraction with ethyl acetate. This was compared to a similar experiment where ethyl acetate was added to the glass tube before storage. The results are given in Figure 3.3.

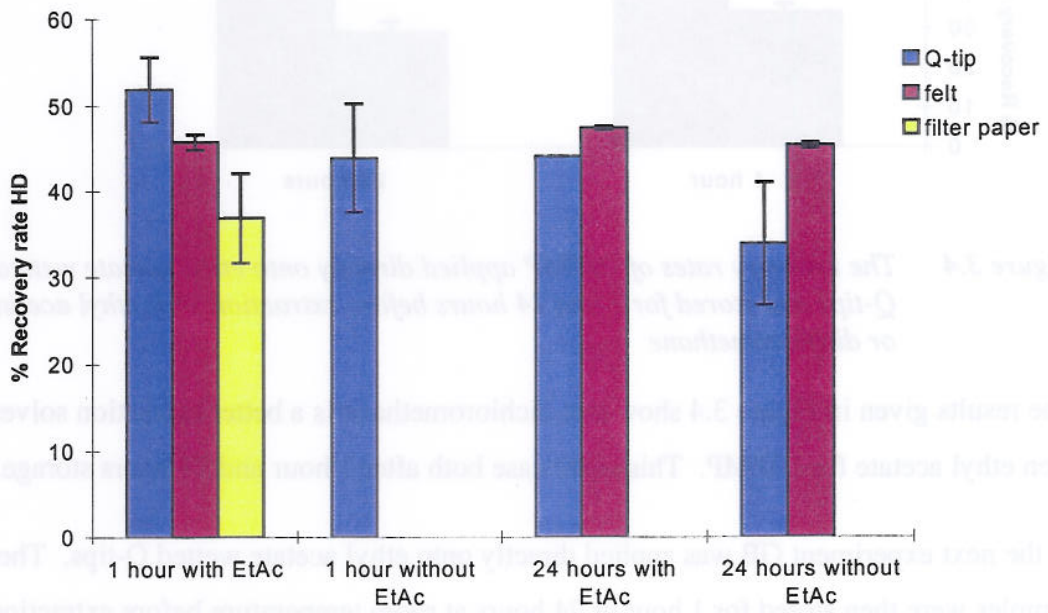

Figure 3.3 *The effect of transportation time and storage with and without ethyl acetate for different sampling media*

The results given in Figure 3.3 show that storing the wipe samples in ethyl acetate before extraction gives a small benefit for the recovery rates of HD. It can also be observed a small decrease in recovery rates from Q-tips after 24 hours compared to 1 hour as can be expected. Felt as sampling media gave almost equal recovery rates from 1 hour and 24 hours storage.

3.2 Sampling of surfaces contaminated with DIPMP and GB

HD has mostly been used in the experiments in this report, but experiments with DIPMP and GB were also carried out. In the first experiment, DIPMP was applied directly onto Q-tips, which were previously wetted with ethyl acetate. The samples were then stored for 1 hour or 24 hours at room temperature before extraction with either ethyl acetate or dichloromethane. The results are given Figure 3.4.

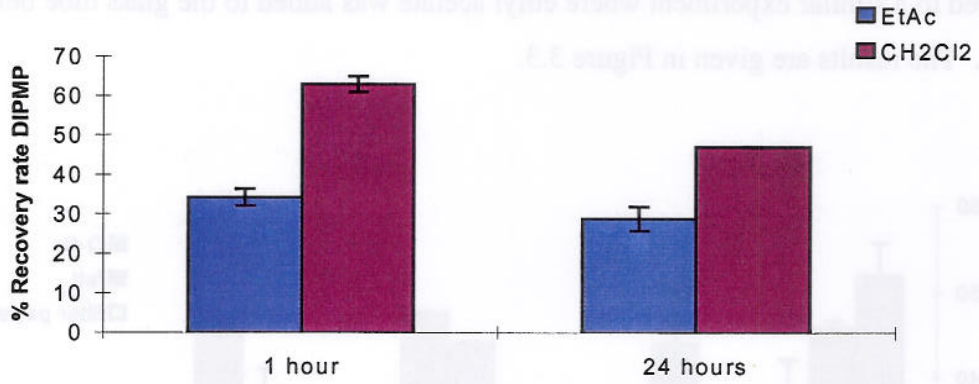

Figure 3.4 *The recovery rates of DIPMP applied directly onto ethyl acetate wetted Q-tips and stored for 1 and 24 hours before extraction with ethyl acetate or dichloromethane*

The results given in Figure 3.4 show that dichloromethane is a better extraction solvent then ethyl acetate for DIPMP. This is the case both after 1 hour and 24 hours storage.

In the next experiment GB was applied directly onto ethyl acetate wetted Q-tips. The samples were then stored for 1 hour or 24 hours at room temperature before extraction with ethyl acetate. The samples were stored both with and without ethyl acetate added to the sample tubes. The results are given in Figure 3.5.

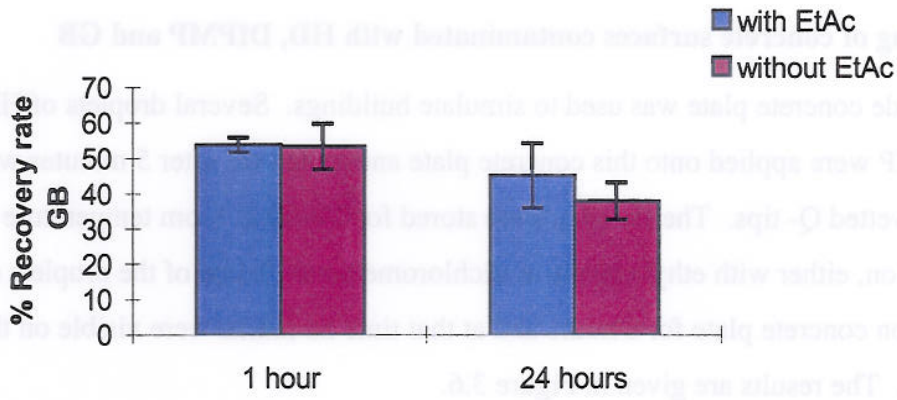

Figure 3.5 *The recovery rates of GB applied directly onto ethyl acetate wetted Q-tips and stored for 1 or 24 hours both with or without ethyl acetate added before storage*

The results given in Figure 3.5 show that there are no significant differences in the recovery rats of GB when the Q-tips are stored for1 hour with or without ethyl acetate. A small but insignificant effect on the recovery rates of storing the sampling media in ethyl acetate is noticed after 24 hours storage.

Several droplets of DIPMP and GB were applied onto a painted metal plate and wiped off after 5 minutes with ethyl acetate wetted Q-tips. The samples were then stored at room temperature for 1 hour or 24 hours before extraction with ethyl acetate. The samples were stored both with and without ethyl acetate added to the samples. The results are given in Table 3.4.

	1 hour storage		24 hours storage	
	GB	DIPMP	DIPMP	
	With EtAc	Without EtAc	With EtAc	Without EtAc
Mean (µg)	221 ± 72	209 ± 46	283 ± 26	297 ± 18
Recovery rate (%)	22	21	28	30

Table 3.4 *Mean ± standard deviation and recovery rates of GB and DIPMP applied onto a painted metal plate, wiped after 5 minutes and stored for 1 or 24 hours before extraction with ethyl acetate*

The results given in Table 3.4 show that storage of wiped samples for 24 hours both with and without ethyl acetate added to the sample gave higher recovery rates of DIPMP then after 1 hour storage. This means that the storage conditions for wipe samples with DIPMP have more or less no effect on the yield of the compound. GB

was only collected after 1 hour storage. The result shows a recovery rate of 22 % with ethyl acetate added to the sample before storage.

3.3 Sampling of concrete surfaces contaminated with HD, DIPMP and GB

A piece of crude concrete plate was used to simulate buildings. Several droplets of HD, GB and DIPMP were applied onto this concrete plate and wiped off after 5 minutes with ethyl acetate wetted Q- tips. The samples were stored for 1 hour at room temperature before extraction, either with ethyl acetate or dichloromethane. Some of the droplets of HD were left on concrete plate for 6 hours and at that time no marks were visible on the concrete plate. The results are given in Figure 3.6.

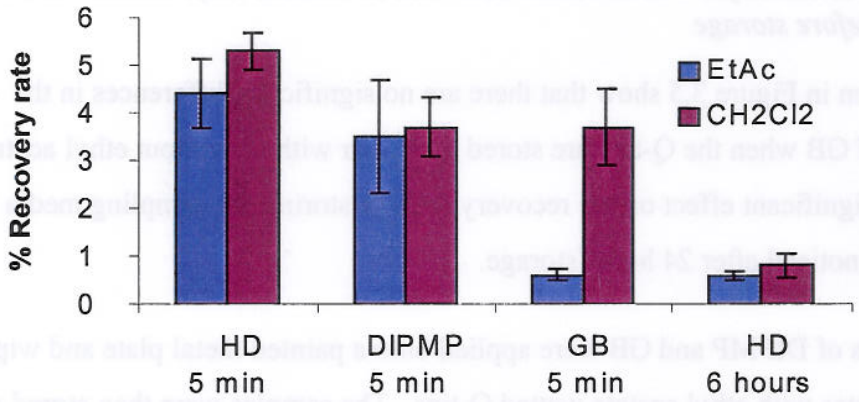

Figure 3.6 The recovery rates of DIPMP, HD and GB applied onto a crude concrete plate and wiped after 5 minutes or 6 hours with ethyl acetate wetted Q-tips. The Q-tips were than extracted ethyl acetate or dichloromethane

The results given in Figure 3.6 show that the recovery rates of HD, DIPMP and GB are less then 6 % after 5 minutes on the crude concrete plate. After 6 hours the recovery rates of HD are less then 1 %. It also shows an increase in recovery rates of GB when using dichloromethane instead of ethyl acetate as the extraction solvent.

To see if the cotton cloth was a better sampling medium then Q-tips for collecting wipe samples from concrete, droplets of HD were applied onto the concrete plate. The concrete surface was wiped after 5 minutes with Q-tips or cotton cloth, which were previously wetted with ethyl acetate. The samples were then stored for 1 hour at room temperature before extraction with dichloromethane or ethyl acetate. The results are given in Table 3.5.

	Q tip		Cotton cloth	
	EtAc	CH_2Cl_2	EtAc	CH_2Cl_2
Mean(μg)	56 ± 9	68 ± 5	63 ± 27	47 ± 23
Recovery rate (%)	4.4	5.3	5.0	3.7

Table 3.5 Mean ± standard deviation and recovery rates of HD applied onto crude concrete plate and wiped after 5 minutes with either Q- tips or cotton cloth wetted with ethyl acetate

The results given in Table 3.5 show no significant differences in recovery rats for HD between Q-tips and cotton cloth.

3.4 Storage of ethyl acetate

Storage of the solvent ethyl acetate in Kimax or Venoject test tubes for a period of time will cause contaminations of the solvents. This can be seen in the GC-MS chromatograms, which show a lot of background peaks (Figure 3.7). The best way to store the solvents in the sampling kit is in an original bottle as small as possible to avoid contamination and evaporation.

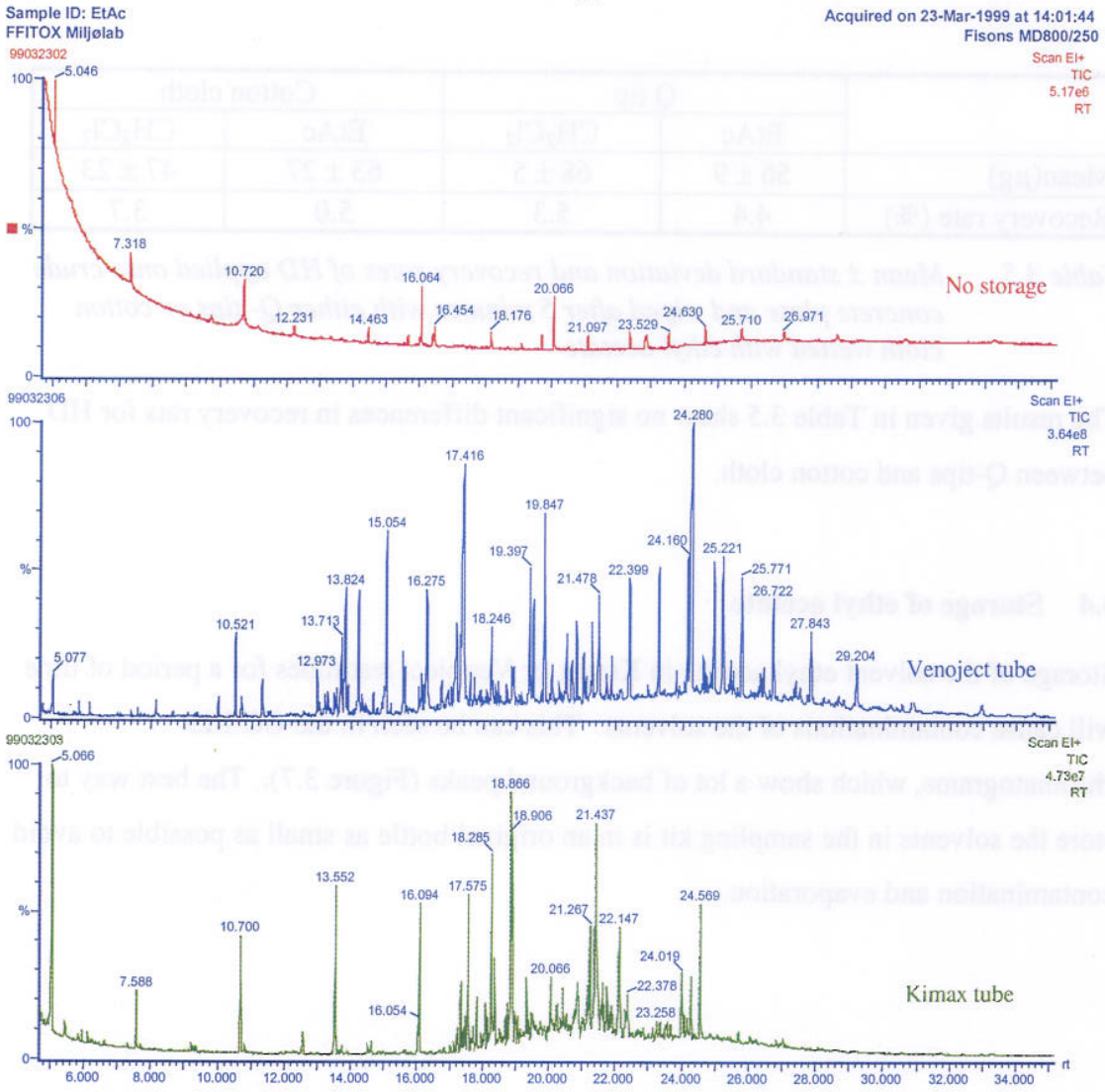

Figure 3.7 Storage of ethyl acetate in Venoject and Kimax tubes for 5 months

4 CONCLUSIONS

The results given in this report show that using a Q-tip for collecting wipe samples from solid surfaces give the highest overall recovery rates for the compounds tested. The Q-tip as a sampling medium is also much easier to use in the field then pieces of felt, filter paper or cotton cloth. Higher recovery rates are also observed by using prewetted sampling media instead of dry. The most versatile solvent for wetting the sampling media is ethyl acetate because of its relatively high boiling point.

Storing the wipe samples in extraction solvent during the transportation to the laboratory did not give any large benefit for the recovery rates of the agents. Dichloromethane as extraction solvent gives the highest recovery rate, especially for DIPMP. The results also show that collecting wipe samples after a long period of time

(6 h, 24 h) gives low recovery. The condition of the solid surface and the length of time after an attack will influence the possibility to verify an alleged use of chemical warfare agents. The chances of positive identification will be greatly enhanced if the droplets or marks of droplet are visible on the surface.

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