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Håkan Carlsson, Ann Kjellström

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Sub-study 4: Vapour sampling and analysis in the project Mine Detection Dogs

implemented by Geneve International Center for Humanitarian Demining.

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Report title

Improvement of vapour sampling and analysis techniques for TNT and related compounds.

Abstract (not more than 200 words)

The purpose of this project was to evaluate the Mechem air sampling system used for mine detection with dogs, Remote Explosive Scent Tracing (REST). When using the REST technique, air samples are collected above the surface of roads and subsequently analysed by specially trained explosive sniffing dogs. The sampling is performed using a pump placed in a backpack. The air is continuously pumped through a filter designed to adsorb the explosives. In this project the sampling was focused on trinitrotoluene (TNT) and related compounds. In addition to the evaluation of the Mechem system, the sampling procedure was improved by development of new filter/adsorbent and sampling equipment. Determination of methods for storage and procedure for the introduction of filter content to the dogs, has also been performed within this project. To verify the content of explosives on the sampled filters, chemical methods for analysis of explosives were developed. The project was a sub-study of vapour sampling and analysis in the project Mine Detection Dogs implemented and funded by Geneva International Center for Humanitarian Demining (GICHD) via Swedish Rescue Services Agency (SRSA).

Keywords

land mines, TNT, mine dogs, filters

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Förbättring av luftprovtagning och analystekniker för TNT och relaterade föreningar.

Sammanfattning (högst 200 ord)

Syftet med projektet var att utvärdera Mechems luftprovtagnings-system som används i samband med detektion av landminor med hjälp av minhundar, Remote Explosive Scent Tracing (REST). När REST tekniken används samplas luftprov in över vägytor och analyseras därefter av specialtränade explosivämnes-sökande hundar. Luftprovtagningen utförs med hjälp av en luftpump som bärs på ryggen. Luften pumpas kontinuerligt igenom ett filter som är designat att adsorbera explosivämne. I detta projekt fokuserades provinsamlingen på trinitrotoluen (TNT) och relaterade föreningar. Förutom utvärderingen av Mechems system har tillvägagångssättet för luftprovtagning förbättrats genom utveckling av filter/adsorbent och provtagningsutrustning. Metoder för förvaring och tillvägagångssätt för att introducera filterinnehållet till hundar har studerats inom detta projekt. För att verifiera innehållet av explosivämne på de provtagna filtren har kemiska analysmetoder tagits fram. Projektet var en delstudie av luftprovtagning och analys i projektet ”Mine Detection Dogs” implementerat och finansierat av Geneva International Centre for Humanitarian Demining (GICHD) via Räddningsverket.

Nyckelord

landminor, TNT, minhundar, filter

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Contents

Objective

The purpose of this project was to evaluate the Mechem air sampling system used for mine detection with dogs, Remote Explosive Scent Tracing (REST). When using the REST technique, air samples are collected above the surface of roads and subsequently analysed by specially trained explosive sniffing dogs. The sampling is performed using a pump placed in a backpack. The air is continuously pumped through a filter designed to adsorb the explosives. In this project the sampling was focused on trinitrotoluene (TNT) and related compounds. In addition to the evaluation of the Mechem system, the sampling procedure was improved by development of new filter/adsorbent and sampling equipment. Determination of methods for storage and procedure for the introduction of filter content to the dogs, has also been performed within this project. To verify the content of explosives on the sampled filters, chemical methods for analysis of explosives were developed.

The project consisted of four modules. The first module discusses the evaluation of the sampling equipment developed by Mechem, *i.e.* filters and air pumping equipment. In the second module new filters with enhanced capacity compared to the Mechem filter was developed. Storage methods of new and sampled filters are recommended in module three. Module four dealt with the optimisation of introduction of filter content to the dogs. Included in the last module was also preparation of filters, with specified content, intended for test and evaluation with dogs. The development of chemical analysis methods was carried out by co-operation with a project funded by the Swedish Armed Forces. Guidelines for storage of filter material and the use of a vapour generator were accomplished through support from a project funded by the Swedish Rescue Services Agency (SRSA). This project was also carried out in co-operation with Department of Analytical Chemistry, Stockholm University.

The report is divided in four modules according to the structure in the project implementation plan.

- Module 1: Explosive Vapour Detection (EVD) sampling. Evaluation of available filtermaterial and sampling equipment/system from Mechem.
- Module 2: Development of new filter material and optimization of sampling conditions.
- Module 3: Storage of filter material

- Module 4: The analysis of filters with dogs: determine the best conditions (supporting NOKSH)

Introduction

In order to measure nitroaromatic explosives in air, adequate sampling methods have to be applied. Different kinds of adsorbents were evaluated for active air sampling. TNT and dinitrotoluene (DNT) are semi-volatile compounds, which means that they exhibit fairly high vapour pressures. The definition of a semi-volatile compound, are any compound that evaporate readily at room temperature. Compounds with high vapour pressure is present to a higher degree in the gas phase while compounds with low vapour pressure is mainly adsorbed to particulate matter in the atmosphere. This could have an effect on the adsorption of the compounds to different adsorbent or filter when using active air sampling. Other parameters affecting the retention of the compounds on filters are the polarity of the substances, type of filter material, sample matrix and the temperature at the sampling location. Compounds with a higher vapour pressure is by definition more volatile and therefore to a minor extent adsorbed to a filter or an adsorbent, compared to compounds which exhibit lower vapour pressure. All DNT-isomers have approximately two orders of magnitude higher vapour pressure than TNT.

Using only a filter without any back-up adsorbent in series behind the filter, increasing the possibility of migration of the compounds adsorbed on the filter into the air stream passing through the sampler, which give rise to a break-through. This is mainly critical for compounds that exhibit a high vapour pressure, *e.g.* DNT. Thus, a loss of molecules adsorbed on the filter can occur and give rise to an underestimation of the concentration of the compounds in the atmosphere. This procedure can yield a too low recovery. However, one should be aware of this problem, principally associated with high-volume sampling. Using a high-volume sampling technique, high performance characteristics of the adsorbent/filter is required to avoid break-through in the sampler.

In order to measure nitroaromatic explosives in air, adequate analytical methods have to be applied. The complete analytical procedure for identifying and quantifying of compounds usually starts with some kind of planning for strategies of sampling and ends up with results, preferably presented with statistical consideration This forms the analytical chain and " a chain is not stronger than it’s weakest link”. Some frequently applied links in this chain can be described by the scheme in figure 1.

“A chain is not stronger than…………
Representative Sampling
Quantitative Sampling
Storage stability
Extraction
Cleanup
Pre-separation
Separation
Identification
Quantitative analysis
Statistical evaluation and presentation
……….it´s weakest link”

Figure 1. Frequently applied links in the analytical chain.

Errors introduced at some point in this chain will automatically be transferred and added to other errors further down the chain, *i.e.* each step is as important as all the others to obtain good results.

Module 1

Explosive Vapour Detection (EVD) sampling. Evaluation of available filtermaterial and sampling equipment/system from Mechem.

To investigate if explosives are retained on the filter used in the Mechem system, an adequate analytical method had to be developed. The material used in the filters is a polyvinylchloride (PVC) coated glass fibre net and the PVC material contains phthalates. Phthalates are used as plasticizers in many plastics and a content of 10% (w/w) is common in many products, but far higher levels are used for some applications. In PVC phthalates are used in concentrations up to 50% (w/w). The high concentration of phthalates is a major problem when developing an analytical method, the major concern is the contamination of the instruments. When developing an analytical method, the first step after the sampling procedure is the extraction, which means that the target compounds have to be desorbed from the sampling matrix, in this case the filter, before the analysis can be performed. A wide variety of extraction methods exist and we have used all the extraction methods available in our laboratory.

Extraction of Mechem filters

To begin with, we extracted the Mechem filters using ultrasonication and Supercritical Fluid Extraction (SFE), respectively. Using ultrasonicated extraction, acoustic vibrations with frequencies above 20 kHz are applied to the sample kept in an organic solvent in a glass cup which is immersed in a water-bath. When these vibrations are transmitted through the liquid, cavitation bubbles with a negative pressure are formed. Chemical compounds and particles are mechanically removed from the matrix surface and adsorption sites, by a shock wave that is obtained when the cavitation bubbles collapse.

SFE is an environmentally friendly and efficient extraction technique. A fluid is regarded as supercritical when both pressure and temperature are above their critical values. A supercritical solvent possesses properties that are favourable for extraction purposes. We used carbon dioxide as a supercritical media.

After the extraction procedure, Gas Chromatography (GC) was used for the final analysis of the nitroaromatics extracted from the filters. These two extraction methods were evaluated before we received the information of the content of phthalates in the filters from the manufacturer. The result we obtained was a complete contamination, of the GC and the SFE instruments, originating from the phthalate content, *i.e.* we could not analyse the Mechem filter using ultrasonication or SFE.

In order to avoid the large content of phthalates, which is a class of compounds designated esters, acid hydrolysis was carried out at the same time as the extraction procedure of the filters occured, using a Soxhlet extractor. The hypothesis was to convert the phthalates to carboxylic acid (phthalic acid) by using hydrolysis (cleavage by water), with a strong acid, *i.e.* hydrochloric acid. Then phthalic acid would separate from the nitroaromatics in the solution due to a difference in solubility and the solution would contain the phthalic acids and the nitroaromatics in two easily separated layers. Soxhlet extraction is performed in an all-glass device, forcing heated solvent to pass the filter a number of cycles, and the filter is in permanent contact with fresh solvent. Soxhlet extraction is a dynamic extraction method, which usually produce high and reproducible yields.

Hydrolysis of an ester in acid solution is a reversible reaction and therefore it is difficult to obtain high yields of a carboxylic acid (phthalic acid). Alkaline hydrolysis is an irreversible reaction, which often results in better yields, but it is impossible to apply on nitroaromatics since TNT is degraded in alkaline solutions. The result obtained was that the reversible chemical reaction was too fast in acid solution, *i.e.* the re-formation of phthalates occurred almost immediately yielding a too high concentration in order to use the GC for the final analysis.

Finally, an extraction method was developed based on Microwave Assisted Extraction (MAE). Microwaves with a frequency of 2450 MHz are mostly used and specially designed instrument for extraction of chemical samples are commercially available. Microwaves have the ability to produce heat by inducing vibrations in substances as a function of their dipole moments, *i.e.* difference in charge distribution in the molecule. Thus compounds with high dipole moments such as water and acetone can easily be heated whereas cyclohexane will remain fairly unaffected. The elevated temperature and pressure is used when extraction is done in closed vessels using microwaves. Thus, nitroaromatics can be dissolved in water in spite of the lower solvating power water possesses, when compared to an organic solvent like acetone.

Water at pH 8 was used as the extraction media. Testing the extraction capacity for nitroaromatics with water in different sample matrices, *e.g.* soil, good results were received. The fat-soluble phthalates were not expected to be extracted from the Mechem filters, using MAE with water as extraction media. In order to isolate the nitroaromatic fraction after the extraction, from phthalates that turned out to be extracted to some extent as well, Solid Phase Extraction (SPE) was used as a clean-up step. Using GC for the final analysis exposed that there were still a major amount of phthalates in the sample extract, which interfered with the detection of nitroaromatics.

Mechem sampling equipment

NOKSH sent a Mechem sampling equipment/system for evaluation and sampling in FOI:s test field. The equipment we received was leaking and measurement of the flow rate with a rotary meter did probably not show the maximum flow rate. The measured sampling capacity was approximately 15 L/min.

Combustion engines do not perform an ideal combustion and numerous compounds besides water and carbon dioxide are emitted. By using a petrol powered sampling equipment *e.g.* the Mechem system, exhaust-related unburned hydrocarbons and particulate matter can be adsorbed by the filter during the sampling procedure and interfere with the chemical analysis and the detection with dogs, as well. To avoid contamination from incomplete combustion battery-operated pumps are preferred.

Module 2

Development of new filter material and optimization of sampling conditions.

Three different new air samplers containing different adsorbents have been constructed. These samplers are intended for use with the REST technique. Analytical methods in order to evaluate the samplers have also been developed. In sampler 1, a distinction between the particulate and the semi-volatile phase is achieved with 2 different adsorbents, sampler 2 and 3 collects both phases using one adsorbent respectively. Compared to sampler 1 and 2, sampler 3 manages a 5 to 8 times higher sampling flow rate. These three samplers and methods for chemical analysis are described in detail below.

Sampler 1

A general outline of the sampler is presented in Figure 2. The sampler consist of a 25 mm glass fibre filter with an aerosol retention of 99,98% for particles greater than 0,3 µm at a flow rate of 3 L/min, in series with two 15 mm x 15 mm cylindrical polyurethane foam plugs (PUF). The glass fibre filter is binder-free borosilicate purchased from Gelman Sciences Inc. (Ann Arbor, MI, US), the cost is approximately US$ 50 / 100 pieces.

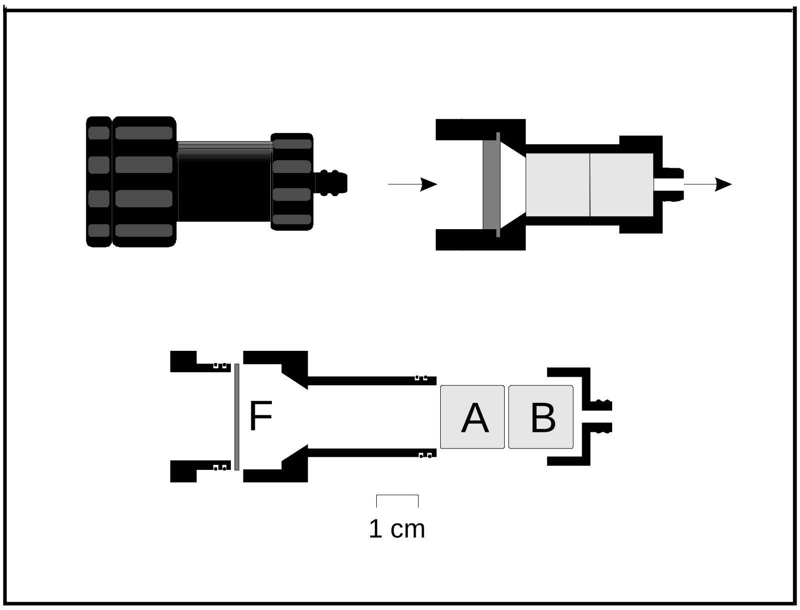

Figure 2: A general outline of sampler 1. F= Filter, A= PUF to trap the semi-volatile phase and B= PUF for breakthrough control

Particulates are collected on the filter, while the semi-volatiles are trapped in the first PUF adsorbent, a second PUF is used for break-through control of the sampling device. The sampler holder is made of anodized aluminium. Semi-volatiles are defined as the fraction of the sample passing through the filter and being retained in the PUF adsorbent, *i.e.* chemical compounds which exhibit a higher vapour pressure in comparison with the compounds adsorbed to particles. The distribution of nitroaromatics between the particulate- and the semi-volatile phases, *i.e* filter and back-up adsorbents, is principally dependent on the vapour pressure of the compounds and thus strongly associated to the molecular weight. All DNT-isomers have approximately two orders of magnitude higher vapour pressure than TNT. Using this sampler, TNT is trapped on the filter and in the first PUF adsorbent in an approximately equal amount, while 2,4-DNT is recovered only in the first PUF adsorbent.

The main drawback with sampler 1 is that both filter and PUF must be introduced to the dog in order to make it possible for the dog to detect both TNT and DNT. This means that filter and PUF must be separated before they are introduced to the dog. The filter is also sensitive for humidity, and thus not recommended for use in humid environments.

Chemical analysis of sampler 1

An analytical method has been developed for the filters and PUFs used for the sampler. As an initial step ultrasonic assisted solvent extraction was evaluated and analysis was performed with a GC equipped with a nitrogen selective detector. A degradation of TNT was observed using ultrasonic assisted solvent extraction, probably caused by surface catalysis on the glass fibre filters. Therefore other extraction methods had to be investigated.

A new extraction method for the filters and the PUF:s using SFE was evaluated and provided good results. An analytical method was then developed by an on-line extraction system combining SFE and High Performance Liquid Chromatography (HPLC). In HPLC a solvent is used to separate the different compounds in the column, prior to detection, instead of a gas which is the case when using a GC for analysis. Using HPLC and SFE separately for sample clean-up and for analysis, a number of sample transfer procedures and solvent reduction steps has to be involved. This is time-consuming and extensive sample handling gives rise to non-reproducible losses and contamination of samples.

Using an automated on-line coupled SFE-HPLC most of these drawbacks were eliminated and furthermore, the sensitivity for the method was increased. The results show that this method is effective, rapid and can be used with sampler 1 for the analysis of explosives in vapour phase. The analytical method is fully automated and allows a complete analysis to be processed in less than 30 min, *ref 1*.

The method has been applied to the analysis of samples obtained from headspace sampling of military grade TNT stored in a dessicator. Sampler 1 was used, with a sampling flow rate of 3 L/min during 10 minutes. The explosives 2,4-DNT, 1,3-DNB and TNT were consistently detected in all the analysed samples and none of the explosives were detected in PUF 2, *i.e.* no break-through was observed. The minimum detectable amount of the individual nitroaromatics, trapped on the filter or the PUF, are in the range of approximately 10–50 ng (10^{-9} g).

Sampler 2

Sampler 2 consists of a solid phase extraction (SPE) column, enclosed in a sampler with a similar structure as sampler 1, with a full length of 10 cm, Figure 3 and 4. The sampler holder is made of anodized aluminium and both particulates and the semi-volatiles are trapped by the adsorbent. The SPE is Abselut Nexus from Varian Inc. (Harbor City,CA, USA), the cost is approximately US$ 130 / 100 pieces. SPE can be used as a combined sampling and clean-up method. A clean-up method is used to isolate the target compounds in one specific fraction, prior to the final analysis. This sampler can be used in humid environments.

Figure 3: Sampler 2 and Mechem filter

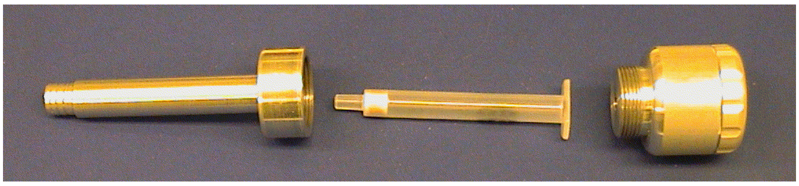

Figure 4: Sampler 2 with the SPE cartridge

The principle for isolating the target compounds after the sampling procedure is to introduce a solvent into the column with adsorbent. If the equilibrium of compounds is strongly orientated, by chemical interaction, towards the stationary phase (adsorbent) the compounds will be quantitatively retained by the solid phase. An initial separation will thus be made, as all non-retained compounds will elute from the column. Further clean-up treatment with other solvents can be carried out in the same way. Finally, the compounds to be analysed are desorbed and eluted, rinsed out, from the column by a solvent with higher solubility properties.

Chemical analysis of sampler 2

A method both for sampling and chemical analysis that is easy to handle has been developed using sampler 2. The sampling device exhibits a combined sampling and clean-up step. The nitroaromatic compounds has been collected on the SPE column with a sampling flow rate of 3 L/min during 3 minutes from headspace sampling of military-grade TNT stored in a dessicator. After sampling, the SPE column was extracted with 0,6 mL of toluene followed by 2 mL of acetone. Then, the extract was concentrated under a gentle stream of nitrogen at 40ºC, in order to remove the acetone fraction before the analysis. Gas chromatography was used for the final separation and quantification of the nitroaromatic compounds. A capillary column was used to obtain a sufficient separation for all the individual compounds. All quantitative analysis of nitroaromatics, are performed with a nitrogen and phosphorus selective thermoionic gas chromatography detector (NPD).

When the method was applied to the analysis of samples obtained from headspace sampling of military-grade TNT, the explosives 2,4-DNT, 1,3-DNB and TNT were consistently detected in all the analysed samples.

Evaluation of sampler 2

The performance of sampler 2 for air sampling of nitroaromatics was evaluated with respect to the break-through volume. For this purpose, two samplers were connected in series and samples were collected at a flow rate set to 3 L/min headspace sampling of military grade TNT. Samples were taken for 6, 8 and 10 min, the latter corresponding to 10 times the air volume contained in the vessel were the military grade TNT was kept. After sampling, both samplers were extracted separately. No traces of nitroaromatic compounds were found in the second sampler, *i.e.* no break-through was detected.

To confirm these results, a new set of experiments was performed. Five sets of three SPE columns put in series in each set were used. Each set were spiked in the first SPE using an organic solvent with 10 ng of nitroaromatic compounds. After spiking, air were pumped for 45 min through the set of samplers at a flow rate of 3 L/min. Another set of three samplers was spiked with the same amount of nitroaromatics but left without pumping any air through. The samplers were wrapped in aluminium foil and stored at –4 ºC. The following day, one of the sets exposed to air pumping was extracted according to the method described above as well as the set not exposed to air pumping.

The remaining sets exposed to air pumping were then extracted every second day. Recoveries ranged from 85 to 100 %, indicating that no break-through had occurred, and there was only slight degradation of the nitroaromatics on the SPE column within the storage time span (10 days) that were tested. This results indicate that the nitroaromatics are stable during transportation if the samples are handled properly, *i.e.* stored dark and in a freezer, see Module 3.

The drawback with sampler 2 is that the maximum sampling capacity is only 3 L/min due to high back-pressure in the SPE cartridge.

Further developed chemical analysis method for sampler 2

An additional method for chemical analysis has been developed for sampler 2, by applying an on-line system for combined clean-up and elution of the sampler directly followed by GC analysis. The purpose of the method was to avoid sample clean-up, or solvent reduction steps, prior to analysis. These steps are labour intensive and can evolve errors in the analysis especially if the compounds are unstable. This on-line method renders a direct analysis, without previous concentration of the solvent used for eluting the compounds from sampler 2. The method uses SFE with carbon dioxide modified (toluene/methyl-tert-butyl-ether) for extraction of the adsorbed nitroaromatics on sampler 2. The sample is directly introduced into the GC utilizing a mechanism for large volume injection, in order to obtain a more sensitive method.

Evaluation of sampler 2 with the further developed chemical analysis

The optimized method has been applied to air samples obtained from headspace sampling of military grade TNT. The developed method shows high reproducibility, low method detection limit and overall robustness. In order to fully validate the method, it will be necessary to study the influence in the field from environmental factors, such as interfering compounds, humidity, wind, and soil characteristics. The minimum detectable concentration for the method is 6 to 36 pg/L air sampled (pg = 10^{-12}g), with a total sampling volume of 10 L.

The analytical method was applied to characterize headspace composition above military grade TNT. Results confirm that 2,4-DNT and 1,3-DNB constitute the largest vapour flux, but TNT, 2,6-DNT, and TNB were also consistently detected in all the samples. In January 2002, personnel from FOI went to Angola bringing the sampling equipment in order to collect samples from real minefields. Unfortunately, the equipment was lost during transport, therefore the samplers have only been tested in the laboratory.

FOI have sent a number of positive and negative filters to NOKSH in June 2002 for NOKSH to use as training material for detection with dogs, Module 4.

Sampler 3

Sampler 3, figure 5 and 6, has been developed, since sampler 1 and 2 have limitation regarding the maximum sampling capacity, 5 L/min for sampler 1 to avoid break-trough and 3 L/min for sampler 2 due to the high back-pressure in the SPE cartridge.

Figure 5: Sampler 3

Figure 6: Sampler 3 with the filter

It is of interest to use a sampling device with high sampling capacity when using the REST technique for area reduction. The benefits using a high flow-rate sampling system are, that the sampling procedure can be speeded up and a larger amount of the explosives can be adsorbed on the filter due to a higher sampling volume per minute.

The use of a sampling device at high flow rate requires high performance characteristics of the adsorbent/filter, to avoid break-through. Sampler 3 consists of a filter (47mm in diameter) and the holder is made of anodized aluminium. The filter is commercially available and consists of a material commonly used as a packing material for HPLC columns, covered with teflon (90:10). Sampler 3 exhibits excellent performance characteristics regarding the sampling capacity for nitroaromatics. The maximum flow rate obtained is 25 L/min using a portable battery operated pump with a maximum flow of 30 L/min. The cost for filters to be used together with sampler 3 is approximately US$ 50/10 pieces (this is a retailer price, a lower price can probably be obtained from the manufacturer when buying larger quantities).

Chemical analysis of sampler 3

A cheap and easy to handle analytical method has been developed to identify the nitroaromatics adsorbed on this filter. In order to extract the nitroaromatics from the filters only a few milliliters of an organic solvent are required, *e.g.* toulene, methanol or methyl-tert-butyl-ether. Using the extraction manifold with vacuum applied, the procedure is very fast, figure 7.

Figure 7: Extraction manifold for filter 3

The extraction procedure is easy to handle, the filter is put in the bottom of the upper glass funnel and the organic solvent is added. Applying vacuum, the organic solvent is forced to pass the filter and the nitroaromatics is eluted from the filter to be collected in a glass vial in the bottom part of the extraction manifold. Prior to analysis, the extract is concentrated under a gentle stream of nitrogen at 40 ºC. The analysis is performed using gas chromatography with a nitrogen phosphorus detector, *i.e.* the same chemical detection system used for analysis of the extracts from sampler 1 and 2. The results of the analysis are verified using an on-line Liquid Chromatography Masspectrometry (LC MS) method.

Evaluation of sampler 3

The performance of the filter has been evaluated with respect to break-through volume. For this purpose, two samplers were connected in series and samples were collected at a flow rate of 11 L/min from headspace sampling of 10 g military-grade TNT stored in a dessicator. Samples were taken for 9 hours, yielding a total sampling volume of 6 m^3 of air pumped through the filters. When analyzing the filters, no traces of nitroaromatic compounds were found in the second filter that indicates no break-through, *i.e.* all nitroaromatics were trapped in the first filter.

The explosive vapour generator, figure 8, was also used for the evaluation of the filter. The concentration of the generated 2,4-DNT and TNT were 0,4 ng/L (ng = 10^{-9}g) and 0,6 ng/L, respectively. Sampling occurred for 14 hours with a flow rate of 11 L/min, yielding a total sampling volume of approximately 9 m^3 with a total amount of the explosives of approximately 4620 ng, without achieving any break through in the sampler.

It is important to use filters with a high capacity for retaining the target compounds during sampling in order to create as favorable circumstances as possible for the explosive detecting dogs. The benefits with sampler 3 are that a large area can be sampled during a short period of time and lower amounts of explosives can be detected due to an enhanced and fast sampling.

Explosive vapour generator

The explosive vapour generator, figure 8, has been constructed in a project funded by Swedish Rescue Services Agency. The aim is to generate specific concentrations of 2,4,6-TNT and 2,4-DNT in order to calibrate explosive vapour samplers and detectors. The system is temperature controlled which permits a wide range of equilibrium vapour concentrations to be generated. Also, the humidity can be varied to simulate different environment. The vapour concentrations are diluted by gas blending to obtain concentrations of TNT and 2,4-DNT as low as 20 pg/L. The generator is able to generate very stable concentrations over a long period of time. The system is equipped with a sampling manifold for air sampling with different air samplers. Reference to be published in July 2003 in the final report of the project funded by SRSA.

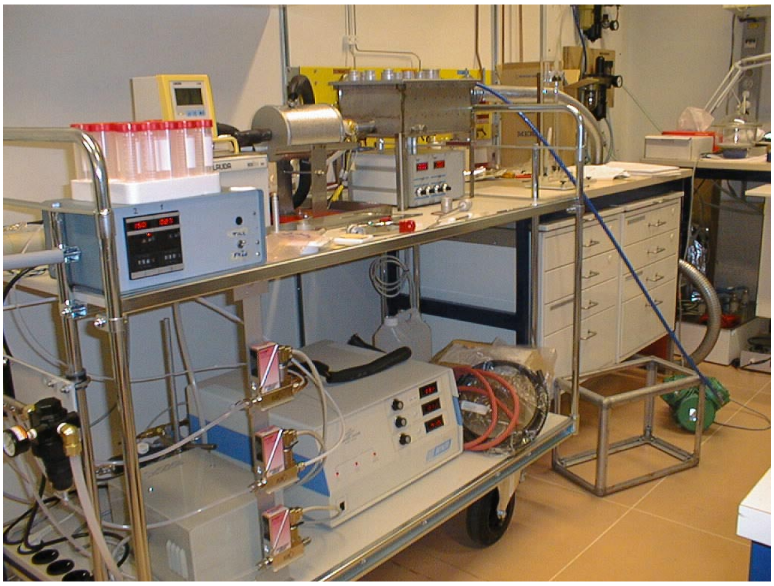

Figure 8: Explosive vapour generator.

Man carried sampling device

A prototype of a man carried sampling device have been constructed, figure 9 and 10, consisting of a 1,7 m aluminum tube, with an adjustable handle, and connected to a battery operated pump. The weight of the tube is less than 0,5 kg and the sampler is attached and released with a single hand snap.

The portable battery operated pump with a maximum flow of 30 L/min weighs 5 kg and can be placed in a backpack. The pump is MCS 30 (certified by European Commission) purchased from SKC Inc. (Eighty Four, PA, USA), the cost is approximately US$ 3000. All three constructed samplers can be used together with this sampling device. The sampling equipment needs further evaluation and development in order to be suited for continuous use in the field.

Figure 9: Portable sampling device with sampler 3 attached for sampling.

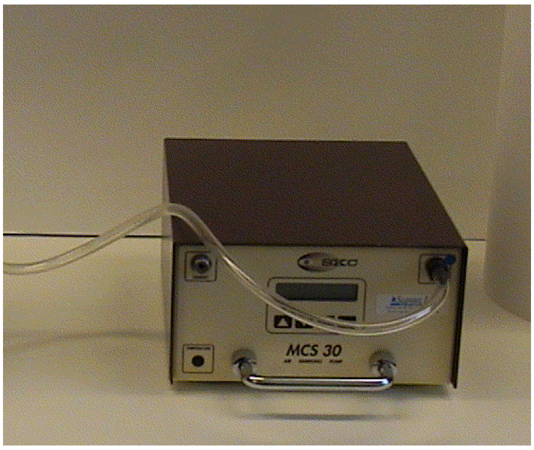

Figure 10: Portable battery operated pump.

Module 3

Storage of filter material

When sampling is performed it is very important to handle the filters in a proper way, in order to avoid contamination by other compounds, degradation of explosives by ultraviolet light (UV-light), *ref 2*, or high temperature. Without proper handling and storage it is no use analysing the filters, as illustrated by the analytical chain. This is also valid for the analysis of filters using dogs.

Filters should be kept in separate containers. Suitable containers are: dark brown glass vials with teflon caps, teflon or steel vials. The filter container should consist of a material that nitroaromatics are less adhesive to than to the filter material. The material should also block UV-light to be suitable for filter storage after sampling.

After the sampling procedure, filters should be kept cold and dark. It is important to keep the filters as cold as possible, preferably in a freezer, to prevent diffusion of the explosives from the filter material. Note from earlier discussion about the vapour pressure of a compound, that increased temperature means increased volatility. The degradation of nitroaromatics is also temperature dependent, since they are thermolabile compounds. Also, TNT is degraded by UV-light forming TNB, and therefore it is important to keep the filters as dark as possible.

The filter materials in all three samplers have been tested for storage stability when holding samples of headspace military grade TNT. No degradation of the sampled compounds was detected, and nitroaromatic amount was stable for weeks if the filters were kept in a freezer and in darkness.

FOI has constructed transportation boxes, figure 11, for samples containing TNT and related compounds in a project funded by Swedish Rescue Services Agency. Insulated aluminium boxes are used, because aluminium both are durable and reflects heat radiation fairly good, the insulation is 5 to 8 cm thick styrofoam. Ice packs are used to keep the box as cold as possible during field sampling. Reference to be published in July 2003 in the final report of the project funded by SRSA.

Figure 11: Insulated aluminium transport box, equipped with wheels and handles.

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Module 4

The analysis of filters with dogs: determine the best conditions (supporting NOKSH)

FOI have sent a number of positive and negative filters to NOKSH in June 2002, both Mechem and new adsorbents (sampler 2). The positive samples were spiked using an organic solvent and pure substances of TNT, 2,4-DNT, 2,6-DNT and TNB as well as military grade TNT. Also positive samples were air sampled from headspace military grade TNT, *i.e.*TNT, 2,4-DNT and TNB. The negative filters were defined as completely new (unopened), with background scent from the laboratory or from different organic solvents. The purpose was to supply NOKSH with material for repetition training of dogs.

A prototype of a thermal device for the samplers has been constructed, Figure 12, with the purpose of introducing the filter content to the mine dogs. Instead of introducing the filters as they are to the dogs, a gentle warm (up to 40°C) air stream will be pumped through the filter in reverse of the sampled direction. The purpose is to introduce a concentrated air sample to the dog. Using a thermal device, desorption of the explosives from the adsorbent will occur due to increased volatility of the nitroaromatic compounds, and thereby a higher concentration of explosives in the vapour phase are obtained. The thermal desorption device is a prototype and has to be further evaluated.

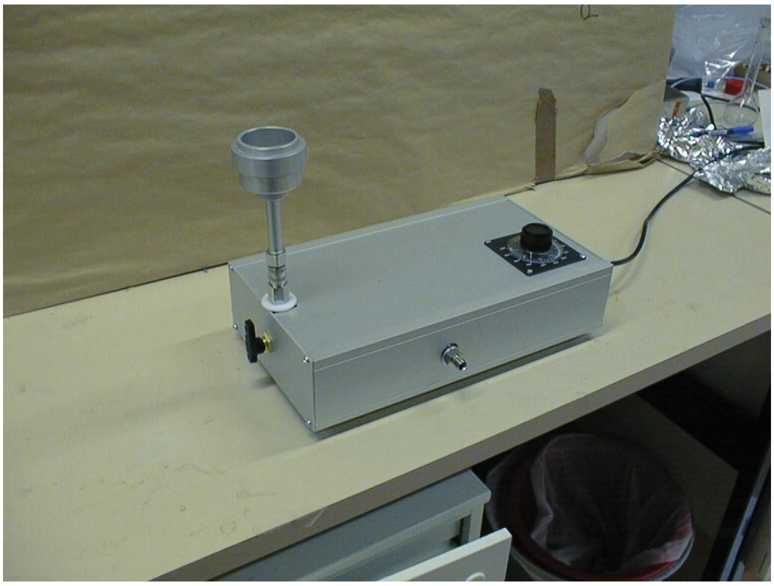

Figure 12: Thermal device with sampler 3 connected.

Results and Conclusions

Module 1

The sampling equipment produced by Mechem has been evaluated and different analytical methods for the Mechem filters have been applied. GC combined with different extraction methods have been used without indicating any detection of nitroaromatics. We find it impossible to analyse the Mechem filters using the different extraction methods, described under Module 1, due to contamination problem in the following chemical analysis. The contamination problem was caused by a high content of phthalates in the filters. To our knowledge we do believe that no commonly used extraction method can be used in order to extract the filters prior to analysis, due to the large content of phthalates.

Mechem filters have been sent from Norwegian Peoples Aid (NPA) in Angola to FOI for chemical analysis. Due to problems as described above, FOI are not able to chemically analyse these filters.

Mine dogs detection capability of TNT and related compounds on the Mechem filters are not possible to verify using the methods for analysis that we have applied.

FOI can not exclude that the phthalates in the Mechem filters influences the detection capability of the dogs as well.

The Mechem sampling equipment that FOI received from NOKSH was malfunctioning, the received equipment was leaking and therefore not possible to evaluate. A point of view is that a pump powered by battery instead of a combustion engine is preferred. With battery-operated pumps interfering exhaust-related unburned hydrocarbons and particulate matter can be avoided during sampling.

Module 2

In order to collect TNT and DNT in air with regard to the use of the REST technique and to render a possibility for chemical analysis of the filters, three new filter systems have been developed. Three different kinds of new air samplers, sampler 1, 2 and 3, have been constructed and evaluated as well as analytical methods. All three samplers can be used together with the prototypes of the battery-operated sampling system and the thermal desorption device.

The samplers have been evaluated using the newly constructed vapour generator. Filters contaminated with a known amount of TNT and 2,4-DNT has been generated and subsequently chemically analysed. No detectable amount of the nitroaromatics migrates through the samplers causing break-through.

The samplers have not been tested in real minefields due to lost equipment during transport.

A number of nitroaromatic compounds have consistently been detected in all analysed air samples from headspace of military grade TNT using the new filters and the sampling system. The identified compounds are: 2,4,6-TNT and 3 other isomers of TNT, 2,4-DNT, 2,5-DNT, 1,3,5-TNB and 1,3-DNB. These compounds can be used as chemical markers in TNT landmine detection.

Using sampler 1, the phase distribution of the nitroaromatics between the particle associated and semi-volatile phases can be analysed separately. Distribution of nitroaromatics between the filter (particulate phase) and the PUFs (semi-volatile phase) is principally dependent on the vapour pressure of the compounds. TNT is trapped on the filter and in the first PUF adsorbent in an approximately equal amount, while 2,4-DNT is recovered only in the first PUF adsorbent. The main drawback with sampler 1 is that both filter and PUF must be introduced to the dog in order to make it possible for the dog to detect both TNT and DNT. This means that filter and PUF must be separated before they are introduced to the dog. The filter is also sensitive for humidity, and thus not recommended for use in humid environments since it holds a glass fibre filter. This filter can be destroyed by exposure to high moisture content.

Sampler 2 uses only one adsorbent for collecting both particulate and semi-volatile phases and are more robust than sampler 1 when used in climate with high humidity. The filter is commercially available and easy to handle.

Both samplers 1 and 2 have an upper limited flow-rate, of 5 and 3 L/min respectively.

Sampler 3 can be subjected to high flow-rates and exhibits benefits in comparison to sampler 1 and 2. The filter can be used at a flow rate of 25 L/min, due to this an increased amount of explosives can be obtained with a shorter sampling time. High flow rates combined with a filter with no break-through gives an increased probability of detecting compounds that occurs in low concentrations.

A prototype of a man carried sampling device have been constructed for proof of function of the filters developed during this project. The sampling equipment needs further evaluation and development in order to be suited for continuous use in the field.

FOI suggests that the prototype of the man carried sampling system together with sampler 3 should be subjected to field trials.

Module 3

Guidelines for storage and transportation of the filters have been produced. Filters should be in separate containers. Suitable containers are: dark brown glass vials with teflon caps, teflon or steel vials.

After sampling, the filters should be kept as cold as possible, preferably in a freezer, to prevent diffusion of the explosives from the filter material. The filters should allow to adopt to a higher temperature, *i.e.* above 0°C, before introduced to dogs for detection of explosives.

In tests for storage stability the filter materials for sampler 1, 2 and 3 shows no degradation of the sampled compounds. Tests with filters holding nitroaromatic compounds, stored dark and in a freezer, showed storage stability for weeks.

Module 4

Equipment and filters prepared with known concentrations of nitroaromatics have been sent to Norway with the purpose of supplying NOKSH with material for repetition training of explosive detecting dogs. Unmarked series of filters for tests with dogs will be available upon request.

A prototype of a thermal device for desorbing the filters has been constructed. The device will introduce a concentrated air sample to the dog and has to be further evaluated.

Scientific quality will be assured by using part of this material together with results from projects funded by the Swedish Armed Forces and the Swedish Rescue Services Agency in upcoming publications.

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