# Effects of Ultrasound Power, Temperature and Flow Rate of Solvent on Decontamination of Sensitive Equipment by Extraction

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## ABSTRACT

The solvent extraction process is regarded amongst other known methods to be applicable for decontamination of sensitive equipment components, especially in cases the components are contaminated in-depth with chemical warfare agents. Viability of the solvent extraction method was evaluated on coupons of butadiene rubber contaminated by sulphur mustard before decontamination by the solvent extraction. The contaminated coupons were extracted in a flow cell, which the solvent (ethoxynonafluorobutane) passed through. Three following specific operational factors, namely the temperature, the flow rate, and the power of ultrasound bath, were assessed for the extent of influencing upon the respective observed extraction efficiencies. The paper describes the results of the evaluation of the solvent extraction effectiveness.

**Keywords:** Chemical warfare agents, decontamination, sensitive equipment, extraction

## 1. INTRODUCTION

Advanced techniques and technologies are lately seen to widely exploit in numerous spheres of life, including these of communication, computational, positioning, observational purposed etc. being based on electronics and/or optics. In cases the contamination of sensitive equipment with lethally toxic agents (CWA) cannot be avoided these components shall be treated with decontamination procedures in order to safe lives of people who handle with the equipment. However, great majority of traditional decontaminating agents and/or procedures can cause damaging the sensitive components, which poses a quite undesirable consequence. In addition, the CWA are capable of considerable penetrating a deeper structure of commonly used plastics or rubbers. Therefore the respective applied decontamination procedures shall be capable of decontaminating the CWA in depth, and not only a surface available CWA fraction.

The solvent extraction technique is a type of physical decontamination, it is relatively fast, non-destructive, and it has satisfying efficiency. The efficiency is rising when it is combined with ultrasonic and with higher temperature. In contrast (for example), adsorption methods (using nanodispersive materials[1]) cannot extracts CWA from structure of materials and plasma method is challenging on logistic (necessary use gases He and $O_2$)[2].

Chemical warfare agent is chemical substance whose toxic properties are used to kill, injure or incapacitate human beings and decontamination of CWA can be defined, as a method essentially involving the conversion of toxic chemicals into harmless products by degradation. Decontamination is based on one or more of the following principles:

(a) to destroy CWAs by chemically modifying these (destruction),
(b) to physically remove CWAs by absorption, washing or evaporation,
(c) to physically screen-off the CWAs so that these cause no damage[3].

Kennedy[4] has recently published a method based on degreasing/washing sensitive components by vapours of fluorinated hydrocarbons or hydrogen fluorinated ethers alone or in a combination with surfactants. The method was evaluated on selected components of typical sensitive equipment being contaminated with non-toxic substitutes of CWA. Scott[5] analyzed in detail corrosive effects of several solvents being applied to decontaminate sensitive components by wash and extraction method. The author used aqueous-alcoholic mixture containing 70 % - 80 % alcohol. Blinov[6] used the methanol.

Kaiser and Haraldsen[7,8] evaluated several hydrofluorocarbons (HFE-7100) that were applied to solvent extraction decontamination. Their processing unit contained decontamination flow-through bath, which was continually eluted by a clean solvent. Decontamination process was assisted by ultrasound (power 500 W and frequency 40 kHz). The solvent from decontamination bath was recycled by passing through a filter and returned to the process. Experiments were performed with CWA surrogates, which were removed satisfactorily. Ang [9], *et al.* applied the devices described above[5] for the study of efficiency of decontamination by solvent for three classes of sensitive equipment. They tested chosen materials - acrylonitrile-butadienestyrene (ABS) cover, ABS interior, silicone rubber keypad and Santoprene™ exterior. The efficiency was 40 % – 98 % and it was dependent on type of

decontaminated material and type of CWA.

The solvent HFE-7200 (ethoxynonafluorobutane) is clear and colorless liquid with faint odor. It is compatible with a wide range of sensitive equipment – the performance of electronic and optical equipment is not affected by immersion in HFE-7200. The principal CWA of concern are sufficiently soluble in HFE-7200 (7 g HD/100 g solvent). HFE-7200 is effective in ultrasonic cleaning baths because it has very low surface tension, which allows it to penetrate small features of the surface[6]. It is nonflammable, nontoxic, and environmentally acceptable[10-12].

The ultrasound has influence on thickness of laminar layer of flowing solvent. The diffusion of matter (from solid phase into liquid phase) is under way across this layer. The thickness of laminar layer depends on frequency of ultrasound bath. Increasing the frequency of ultrasound leads to a decrease of laminar layer thickness[13].

Temperature has a significant influence on the rate of extraction. Temperature influences primarily diffusion parameters (coefficients)[14,15], which characterize transfer of matter from solid surface to liquid and transfer of matter from laminar layer to main flow of solvent. Furthermore, it influences on the viscosity of solvent and solubility CWA in solvent.
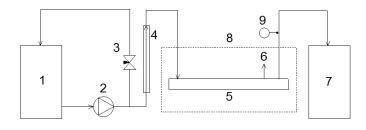
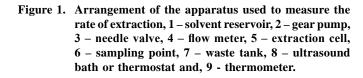## 2. EXPERIMENTAL
### 2.1 Materials Used
- Ethoxynonafluorobutane (HFE-7200) was purchased from 3M Česko Prague, Czech Republic
- Butadiene rubber coupons (tyre-tread stock No. 165) were delivered by Mitas Zlín, Czech Republic
- Sulphur mustard (purity ca. 92 per cent; hereafter also HD) was purchased from the Laboratory of training, analytical and supply center RCHBO, Čereňany, Slovakia.

### 2.2 Determination of the Solvent Extraction Kinetics

Determination of the solvent extraction kinetics was arranged to acquire a deeper insight into the respective relations amongst the observed progress of the extraction process in time and three selected operational parameters, namely (i) flow-rate, (ii) temperature, and (iii) energy output of the used ultra-sound source (bath).

Kinetics of the solvent extraction was measured using the experimental apparatus arrangement as shown in Fig. 1. The fresh solvent (HFE-7200) was delivered by a gear pump (2) from a solvent reservoir (1) through flow meter (4) into the extraction cell (5) and then into the waste tank (7). The extraction cell consisted of two parts, as shown in Fig. 2. The inner space of the extraction cell was defined by the area of an excavation in its bottom part and inner height of 5 mm. The coupon (50 mm × 50 mm × 2 mm) was contaminated by droplets of the HD at the average contamination of 2.54 g.m^{-2}, individual droplet size was 1 μl (the butadiene rubber is one of many materials which are used for making sensitive equipment. We chose this material because the HD easily penetrates into structure of this material). The HD was chosen as representative of CWA because it can penetrate into majorities material (in comparison with V and G agents) and his removing/decontamination is more complicated.
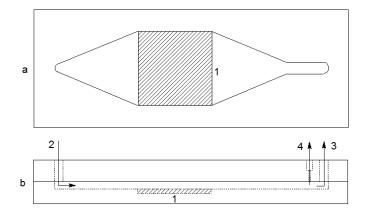


**Figure 1.** Arrangement of the apparatus used to measure the rate of extraction, 1 – solvent reservoir, 2 – gear pump, 3 – needle valve, 4 – flow meter, 5 – extraction cell, 6 – sampling point, 7 – waste tank, 8 – ultrasound bath or thermostat and, 9 - thermometer.



**Figure 2** Design of extraction cell assembly, a – bottom part (view from above), b – bottom and upper part (side view), 1 – butadiene rubber coupon, 2 – inlet of solvent, 3 – outlet of solvent and, 4 – sampling point.

Then after 60 min the contaminated coupon was placed into the bottom part of the extraction cell to be treated by the solvent extraction. Two flanged necks (for inlet and outlet of solvent) were placed to the upper part of extraction cell. The sampling point was located in the upper part of the cell assembly. Extraction cell was placed in ultrasound bath or in thermostat to measure the dependence of the observed extraction rate either on the ultrasound power or temperature. The samples of solvent were taken for analyses from the sampling point in defined time intervals. Obtained samples were quantitatively analyzed by using gas chromatograph equipped with flame photometric detector (with sulphur filter) under thermal conditions at 250°C.

The solvent can be reused if it is filtered through layer of powder mixed oxide-hydroxide Ti/Zn with Ag^{+} silica gel (1:1). The powder is decontaminated by 10 per cent solution of calcium hypochlorite after filtration.

## 3. RESULTS AND DISCUSSION
### 3.1 Influence of Flow Rate on the Extraction Process

The dependence of the HD extraction rate on the flow rate of extraction solvent was measured at three flow rates: 0.1667 ml.min^{-1}; 0.3054 ml.min^{-1}, and 0.4444 ml.min^{-1}. The time of extraction was 45 min and quantity of solvent was 100 ml, 150

ml or 270 ml. Obtained results are presented in Fig. 3. The HD concentration in solvent rapidly increases just after the beginning of the extraction process. After reaching the local maximum the concentration slowly decreases. At higher flow rates the decrease of concentration is faster and the observed local maxima on the respective extraction curves are reached earlier.

The location of maximum at extraction curve on Fig. 3 shows the end of dissolving of droplets by the solvent HFE-7200. The concentration of the HD decreases after this point due to slow HD desorption from the coupon subsurface layers. The second maxima in time $t = 10$ min are caused by higher amount of HD in upper layer of rubber. The shape and the progress of extraction of curves is the similar for all experiments.
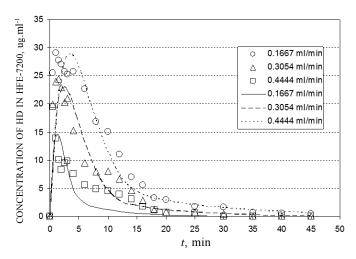


**Figure 3. Dependence of concentration HD in the solvent at the time of extraction and flow rate of solvent (25 °C, without ultrasound); points indicate experimental values and solid lines calculated data.**

The experimental data were fitted with calculated values obtained using mathematical model by least squares method. The mathematical model described processes during the extraction. The overall average decontamination efficiency was 90.99 per cent.

### 3.1.1 Mathematical Model

The butadiene rubber coupon is penetrated with the HD when exposed to droplets of that agent. The absorbed amount of the HD in the rubber depends upon the exposure time, temperature and overall area, which the HD droplets occupy on the coupon surface. The diffusion of that agent across the rubber can be described with the respective diffusion parameters, i.e. diffusion coefficient and maximum attainable concentration of the HD in the rubber. By using these parameters the distribution of the HD in the rubber structure can be estimated at the moment the extraction is started.

Within the extraction stage a surface available fraction of the HD droplets is dissolved into the solvent passing over the interface between the HD liquid phase and solvent after putting the sample together with the extracting solvent in the cell. While the HD surface available fraction is dissolved at the interface "droplet – solvent", the sessile agent penetrates

continuously until the HD liquid phase is completely removed from the coupon surface. The rate of the HD dissolving into the solvent depends on several parameters, as follows
(a) the HD maximum attainable concentration in the solvent,
(b) diffusion coefficient, which characterizes the HD transfer through a laminar layer of solvent,
(c) flow rate of solvent in the cell (which influences a thickness of laminar layer and coefficient of variations of solvent in the cell),
(d) concentration of the HD in main stream of solvent in the cell and
(e) area (of diffusion).

The HD passes into the solvent main stream from the sample after dissolving of the liquid phase of HD. This process is controlled by concentration gradient. It is dependent on diffusion coefficient of the HD in sample and laminar layer of the solvent.

The numerical method of solving Fick's equation for one-dimensional diffusion over combined media[16] was used to analyse the acquired experimental data.

The concentration of HD (in the main stream at the output of the extraction cell) was calculated by the following equation

$$c_{HD,(\tau+\Delta\tau)} = c_{HD,\tau} + D_{HD\text{-}sol,t} \frac{\Delta\tau}{(\Delta x)^2}(c_{Sol,n,\tau} - c_{HD,\tau})S_k \frac{n_k}{V_c} - \frac{Q}{V_c}c_{HD,\tau}\Delta\tau \quad (1)$$

where $c_{HD,(\tau+\Delta\tau)}$ is the HD concentration in main solvent stream at an extraction time $(\tau+\Delta\tau)$, symbol $c_{HD,\tau}$ stands for the HD concentration at time $\tau$, $\Delta\tau$ means a time step of numeric integration, $D_{HD\text{-}sol,t}$ is a coefficient characterising the HD diffusion through the solvent laminar layer at a temperature $t$, $\Delta x$ is a longitudinal step of the numerical integration, symbol $c_{Sol,n,\tau}$ means the HD concentration in last (numerical) segment of the solvent laminar layer, $S_k$ stands for a surface of a spherical cap of the HD droplet occupying the rubber surface, $n_k$ is number of droplets deposited onto the rubber, $V_c$ stands for an inner volume of the extraction cell, and symbol $Q$ is volume flow rate of the solvent through extraction cell.

The diffusion parameters were calculated using by mathematical model and characterized HD concentration evolution in time:
- diffusion coefficient for spreading of HD in rubber $D_{rub,t}$ (20 °C) = $5,095 \times 10^{-7}$ cm$^2$.s$^{-1}$;
- diffusion coefficient for spreading of HD in solvent $D_{HD\text{-}sol,t}$ (20 °C) = $5,664 \times 10^{-5}$ cm$^2$.s$^{-1}$;
- diffusion coefficient for desorbing of HD from rubber $D_{rub\text{-}sol,t}$ (20 °C) = $2,099 \times 10^{-6}$ cm$^2$.s$^{-1}$;
- maximum concentration of HD in the rubber $c_{max,rub}$ (20 °C) = $7,486 \times 10^{-2}$ g.cm$^{-3}$.

The difference between the curves measured at various flow rates is given, in particular, by the thickness of the laminar layer. This can be mainly ascribed to the character of the flow, which controls the thickness of the laminar layer. Significant reduction of this layer thickness could be supposed as the flow rate rises up. Another reason for that observation is a mass exchange since with rising flow rate a greater amount of the HD is brought out of the cell due to its elution.

## 3.2 Influence of Temperature on the Rate of Extraction

The dependence of extraction rate of the HD on temperature was determined for three values of temperature (25 °C, 35 °C, and 50 °C). The value of the flow rate of solvent through extraction cell was constant (0.3054 ml.min⁻¹). The time of extraction was 45 min and quantity of solvent was 150 ml. The results are presented in Fig. 4. It is clear that the increase of temperature speeds up the extraction. Maximum of extraction curves is achieved earlier, and its value is higher than for extraction at laboratory temperature.
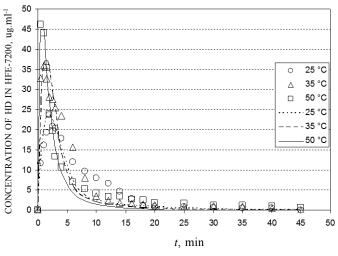


**Figure 4. Dependence of concentration of the HD in the solvent at the time of extraction and temperature of solvent (flow rate 0.3054 ml.min⁻¹, without ultrasound).**

The influence of temperature on extraction was considered in several ways in addition to the influence on the diffusion parameters. The values of all diffusion parameters were increasing with rising temperature. Increase of temperature also increases the solubility of HD in the solvent. With increased temperature also the viscosity of solvent decreases. The viscosity is included in the calculation of Reynolds number and therefore indirectly affects the thickness of the laminar layer. The overall average decontamination efficiency was 88.95 per cent.

## 3.3 Influence of Ultrasound Power on Rate of Extraction

The dependence of extraction rate of the HD on the ultrasound power was evaluated using three values of ultrasound power (64.5 W; 129 W, and 215 W). The value of flow rate was 0.1667 ml.min⁻¹ for all measurements. The time of extraction was 45 min and quantity of solvent was 270 ml. Results presented in Fig. 5 show that ultrasonic extraction has maximum of curve reached earlier and the descending part of the extraction curve is steeper when compared with extraction without ultrasound at the same flow rate of extraction solvent.

The effect of ultrasound on the solvent extraction efficiency could be considered in two ways. The first one is a capability of the acoustic waves to decrease a thickness of laminar layer, and the second is its ability to increase the rate of diffusion of the HD in rubber matrix and diffusion of the HD
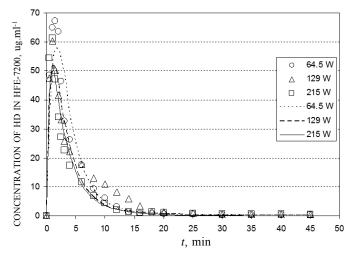


**Figure 5. Dependence of concentration HD in the solvent at the time of extraction and ultrasound power (25 °C, flow rate 0.1667 ml.min⁻¹).**

through the solvent laminar layer.

The extraction curves are similar for all values of ultrasound power exhibiting only minor deviations (Fig. 5). The ultrasound influences speed of extraction, but it is not depend on ultrasound power. The overall average decontamination efficiency was 90.12 per cent.

## 5. CONCLUSIONS

Decontamination by the solvent extraction was evaluated for three elected operation factors, namely the flow rate of the applied solvent passing over the contaminated surface, the temperature of extraction and the applied ultrasound power. The respective experiments were performed on butadiene rubber coupons contaminated with the HD. All investigated operational factors positively influenced the respective observed extraction rates. Increase of the flow rate of the solvent decreases the thickness of the laminar layer, which makes the extraction process faster. In the applied range of operational conditions the flow rate was found as the most important factor contributing to the overall decontamination efficiency. Temperature affects not only the thickness of the laminar layer, but also the diffusion parameters of the extraction. Also, the ultrasound accelerates the extraction, but extraction efficiency isn't significantly dependent on the power output of the used ultrasonic bath. The respective effects of the temperature and/or ultrasound power were recognised as somewhat slighter. But still these operational factors cannot be omitted.

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