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Optimisation of solvent desorption conditions for chemical warfare agent and simulant compounds from Porapak Q^{TM} using experimental design

Part 2: Extraction of sulphur mustard from steel and glass Porapak^{TM} tubes

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Abstract

The vesicant chemical warfare (CW) agent sulphur mustard remains a hazard to personnel involved in demilitarisation activities. Sampling tubes containing Porapak Q^{TM} are used to measure personal exposure to sulphur mustard vapour. Presented here is an evaluation of the solvent desorption parameters employed to remove sulphur mustard from steel and glass tubes containing Porapak Q^{TM}. Statistical experimental design was used to elucidate the influence of solvent type, tube type, solvent volume and sonication time on sulphur mustard recovery. The order of increasing recovery was established as *iso*-octane < hexane = isopropyl alcohol. The same degree of sulphur mustard is recovered on both steel and glass tubes using hexane or isopropyl alcohol, with hexane exhibiting quantitative recovery. The sorbent mass (50 mg) should be increased when using steel tubes as breakthrough has been demonstrated. Given the inert nature of hexane towards sulphur mustard, its favourable chromatographic properties for splitless injection, and its greater recoveries, this solvent should be used for elution of Porapak Q^{TM} tubes for quantitative analysis of sulphur mustard.

Keywords: Sulphur mustard; Porapak Q; Solvent desorption; Experimental design

1. Introduction and aims of investigation

Sulphur mustard (which has the NATO military designation H), is the common name for the liquid vesicant (blister) agent 1,1-thiobis(2-chloroethane). It causes large painful blisters filled with colourless to yellowish coloured liquid, which are formed at the points of dermal contact [1]. Effects may not be seen until 24 h after exposure.

H was first synthesised by Despretz in 1822 [2] and was first used by the Germans against allied troops near Ypres in Belgium in 1917. Since WW1, H has been stockpiled by many nations and used in further conflicts including the Iran–Iraq war [3–5].

Continual development of effective medical countermeasures, development of protective clothing and assessment of exposure necessitate trace detection techniques. Several methods have been used to monitor atmospheric concentrations of H, which focus on its collection on a suitable sorbent material, such as Tenax TA^{TM} or Porapak Q^{TM}, prior to analysis. The H may then be desorbed from the tube using either thermal desorption (TD) [6–7] or solvent desorption (elution). Trace level determination of H is accomplished by thermal desorption at Porton Down [7]. However, the 'one shot' nature of this technique is a disadvantage [8]. TD instrumentation is now available to allow the recollection and reanalysis of samples, which will solve this problem [9].

Trials of equipment conducted at Dstl, Porton Down require replicate analysis of samples. To meet this requirement, H is currently analysed by gas chromatography with a flame photometric detector (GC-FPD). Historically H has been extracted from the sorbent tube with 4 ml of propan-2-ol (IPA) and a sonication time of 10 min for a glass tube. Sonication is not employed for steel tubes and eluate is collected

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in a pre-weighed vial. The use of alcohols for extraction of chemical warfare (CW)-related samples have occasionally lead to the formation of esters, which is undesirable [10]. Also, IPA is not ideal when non-polar columns are used for analysis with splitless injection. Therefore, the aim of this investigation was to develop and optimise an extraction method of H from Porapak Q^{TM} tubes. Three solvents were investigated, IPA, hexane and 2,4,4-trimethylpentane (*iso*-octane), with different elution volumes on both steel and glass tubes. The sonication time required for the extraction from glass tubes was also investigated.

Examination of these parameters allowed a comparison of the behaviour of H towards its simulant compound, methyl salicylate (MS), and the report was published in a previous paper [11].

IPA was evaluated as it has been traditionally used to elute Porapak Q^{TM} tubes at Porton Down. Hexane was investigated as a possible alternative to IPA for reasons mentioned above. *iso*-octane was evaluated due to its excellent chromatographic properties and relatively high boiling point potentially improving sample stability through reduced evaporation.

2. Experimental methodology

2.1. Mathematical model

Two separate mathematical models were developed in this study; a model for the recovery of H from Porapak Q^{TM} using glass tubes, and a model using steel tubes.

The effect of three variables which potentially influence recovery of H from Porapak Q^{TM} were considered for the experimental design. Solvent type, solvent volume and sonication time, in the case of glass tubes, were considered for each combination of solvent and tube type. As two of the parameters were categorical variables, a full factorial design (2^3) could have been constructed. This would have resulted in 96 experiments being necessary to characterise the desorption behaviour of H. Thus, six central composite designs (CCDs) were constructed; a design for each combination of tube type and solvent type. Although this did not reduce the number of experiments performed (102), the CCD provided a clear interpretation of the effects of altering variables on the response (% recovery).

The CCD consists of a star design imposed through the centre of a factorial design. The principles and application of CCD are explained elsewhere [12]. An α-value of 1.414 was used in the two parameter design and 1.633 in the three parameter design to ensure rotatability and orthogonality as calculated by Eq. (1). The upper and lower limits of each factor were placed on the axial points of the design.

$$\alpha = \pm(N_F)^{1/4} = \pm 1.414 \text{ or } 1.633 \quad (1)$$

where N_F is the number of experiments in factorial portion of design.

Table 1
Three-factor CCD used to investigate desorption behaviour of H from glass tubes

Factor	Levels				
	−1.631	−1	0	+1	+1.631
x_1 solvent volume (ml)	2.0	2.8	4.0	5.2	6.0
x_2 applied H mass (μg)	0.4	1.3	2.7	4.1	5.0
x_3 sonication time (min)	2.0	3.6	6.0	8.4	10.0

A CCD was created for glass tubes to consider solvent volume, sonication time and applied H mass (three parameter CCD). A second CCD was used for steel tubes to investigate the influence of applied H mass and solvent volume. Table 1 details the experimental domains used for each CCD. The form of the CCD models can be described in a generalised form by Eq. (2).

$$Y = \beta_0 + \sum \beta_j x_j + \sum \beta_{jj} x_j^2 + \sum \beta_{jk} x_j x_k \quad (2)$$

where Y is the response of system; $x_{j,k}$, variable of system; β_0, β_j, β_{jj}, β_{jk}, regression coefficients for constant, linear, square and interaction terms, respectively.

Regression coefficients are calculated by fitting the values of experimental parameters to the least squares regression line. A quadratic equation or an equation containing only significant terms results. This can then be used to predict the response of the system at given levels of experimental factors.

2.2. Reagents

The H stock was prepared in-house with a purity of 99%. IPA and hexane (distol quality) were supplied by Fisher Scientific (UK) and used without further purification. *iso*-octane was purchased from BDH Laboratory Supplies (UK). Steel tubes were packed in house with 50 mg Porapak Q^{TM} (50/80 mesh) supplied by Supelco, UK Glass Porapak Q^{TM} tubes (100/50 mg) were purchased from SKC, UK and used without further conditioning.

2.3. Spiking of Porapak Q^{TM} tubes with H

Stocks of 100 and 200 μg ml^{-1} of H in *iso*-octane and hexane, respectively, were used to spike the tubes. Regarding IPA, the tubes were spiked with the hexane stock first and then eluted with IPA to minimise the chance of reaction between H and IPA. Each tube was connected to a personal sampling pump with a flow rate of 750 ml min^{-1}. The pump was initialised and stock injected onto the packing to give the desired H mass on-tube. The pump was left running for 30 s, then the tube removed and the caps replaced. Once the tubes were spiked, they were eluted following the design quantities and analysed by GC-FPD. Note: although adequate for this experiment, a more realistic spiking method has been adopted by our laboratory now. Spiking tubes with a vapour loading rig is used as reported previously [11,12].