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# Optimisation of recovery protocols for double-base smokeless powder residues analysed by total vaporisation (TV) SPME/GC-MS



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## ABSTRACT

The investigation of explosive events requires appropriate evidential protocols to recover and preserve residues from the scene. In this study, a central composite design was used to determine statistically validated optimum recovery parameters for double-base smokeless powder residues on steel, analysed using total vaporisation (TV) SPME/GC-MS. It was found that maximum recovery was obtained using isopropanol-wetted swabs stored under refrigerated conditions, then extracted for 15 min into acetone on the same day as sample collection. These parameters were applied to the recovery of post-blast residues deposited on steel witness surfaces following a PVC pipe bomb detonation, resulting in detection of all target components across the majority of samples. Higher overall recoveries were obtained from plates facing the sides of the device, consistent with the point of first failure occurring in the pipe body as observed in previous studies. The methodology employed here may be readily applied to a variety of other explosive compounds, and thus assist in establishing 'best practice' procedures for explosive investigations.

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## 1. Introduction

In recent decades, improvised explosive devices (IEDs) have become an increasing topic of public concern, with high-profile incidents such as the Bali (2002), London transport (2005), Boston Marathon (2013) and Brussels (2016) bombings garnering mass international attention. Although the majority of media coverage has focussed on large-scale incidents, there has also been a rise in explosive incidents involving smaller devices such as pipe bombs. This is particularly the case in the United States, where pipe bombs are considered to make up the vast majority of IED encounters [1,2]. These devices can be easily constructed from everyday materials, and the containment provided by the pipe can produce a large explosive effect using readily obtained low explosive powders such as black powder, black powder substitutes (e.g., Pyrodex<sup>®</sup> and Triple Seven<sup>®</sup>) and smokeless powder.

In the United States, pipe bombs frequently employ smokeless powder as the explosive charge. Smokeless powders are a class of nitrocellulose-based propellants designed to produce minimal solid residue upon firing, and can be categorised as single-

double- or triple-base depending on their composition. Single-base powders rely solely on nitrocellulose as the energetic component, while double-base smokeless powder (DBSP) also contains nitroglycerin for increased detonation velocity [3–5]. Triple-base powders additionally employ nitroguanidine to lower the flame temperature and reduce barrel erosion, although these formulations are restricted to large calibre munitions and are hence rarely encountered in IEDs [6,7]. All three varieties of smokeless powder may also contain additives, such as diphenylamine or ethyl centralite, that act as stabilisers, plasticisers, opacifiers or flash suppressants [8].

Smokeless powders are favourable for use in IEDs in the United States due to their ready availability, with 10 million pounds (4500 t) produced commercially each year [9]. They are also relatively powerful; decomposing at rates of up to 1000 m per second; and can be purchased loose at sporting goods stores in quantities of up to 25 pounds (11 kg) [7,9]. Consequently, smokeless powders comprised over 20% of explosive incidents involving low explosives reported to the United States Bomb Data Centre between 2008 and 2014 (J. Clyburne, United States Bomb Data Centre, personal communication, 2015). The investigation of these events relies upon the recognition and recovery of pipe bomb container fragments at the scene followed by visual/microscopic examinations, culminating in the detection and identification of residues on the fragments. Post-blast material, including container

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fragments and nearby witness materials, may contain either particles of the explosive and/or invisible residues. Particles are not encountered in every case, hence the extraction of post-blast residues from surfaces is common.

To this end, a large volume of research has focussed on developing highly sensitive and selective instrumental methods for the analysis of explosive materials. However, the success of these methods is largely dependent on the sampling method, storage conditions and extraction parameters employed *prior* to instrumental analysis [10–12]. Adequate research to develop appropriate sampling and handling procedures is thus of equally critical importance.

A common sampling method for explosive residues, particularly on large, non-porous surfaces, is the use of swabbing techniques. A number of studies have thus evaluated various swabbing materials, solvents or extraction procedures in the recovery of both organic and inorganic explosives [13–19]. The findings of these studies have been varied, with the best swabbing media and wetting or extraction solvents often differing according to the recovery surface or target analytes utilised [15,16]. Investigations have also been conducted regarding the stability of explosive residues stored under different conditions. These inquiries have established that volatile explosives such as TATP may rapidly evaporate at room temperature, while nitroaromatics such as TNT are prone to photo-transformation if left exposed to light [13,20,21]. Suitable storage conditions must be determined for such samples in order to preserve their evidential value.

Despite a number of studies concerning the sampling, storage or extraction of explosive residues, there is a lack of research investigating particular combinations of these factors. Song-im et al. investigated a combination of swab types and solvents for the recovery of explosive residues on different substrates; however, the same extraction parameters were employed for all samples, and no analysis was made of the effect of different storage conditions [15]. Similarly, DeTata et al. examined a combination of swab types, solvents and agitation methods for the recovery of explosive residues, but utilised only a single swab type and solvent to investigate the stability of residues stored at different temperatures [13]. This univariate, one-at-a-time approach fails to take into account potential interactions between the factors, and the effect that these may have on explosives recovery. Additionally, studies to date have relied solely upon visual assessment of the acquired data. Interaction effects may not be readily evident from the raw data, and can thus be overlooked when relying on manual inspections.

Effective optimisation requires statistical methods or algorithms to identify and model interactions within the dataset. One such approach is the use of experimental design methods such as a central composite design (CCD). This is a multivariate technique that models the relationships between several explanatory factors, such as sampling or storage parameters; and a dependent response, such as the consequent explosives recovery [22,23]. The resultant data can be used to determine the factor levels that will produce a target response, as well as determining the significance and effect of any factor interactions [24]. CCDs are particularly desirable due to their high efficiency; providing the necessary information in a minimal number of experiments [22]. Additionally, unlike many other experimental designs, CCDs are capable of modelling curvilinear variable effects [25,26]. Recent studies have successfully utilised CCDs to optimise the extraction and instrumental analysis parameters of propellant or nitroaromatic explosive residues [27–29]. In spite of these findings, the broader capability of experimental design to investigate initial factors such as appropriate sampling and storage methods remains unexplored.

In this study, a CCD was employed to investigate sampling,

storage and extraction procedures for the recovery of DBSP residues analysed using total vaporisation (TV) SPME/GC–MS. This method has been demonstrated as offering greater sensitivity than liquid injection or headspace or immersion SPME for a variety of analytes such as nicotine, cotinine and components of smokeless powder on steel pipe bomb fragments [30,31]. The optimised parameters were then applied to post-blast residues deposited on witness materials following detonation of a pipe bomb device.

## 2. Materials and methods

### 2.1. Materials

Acetone (analytical grade, Fischer Scientific) was used as received. Alliant Red Dot double-base smokeless powder was obtained from Gander Mountain (Indianapolis, IN), and a solution of this powder (1.022 g in 500 mL) prepared in acetone. PVC piping was sourced from Home Depot and low carbon galvanised steel sheets from Grainger Industrial Supply (Indianapolis, IN). SPME fibres were purchased from Sigma Aldrich, and SPME vials and caps from Gerstel.

### 2.2. Optimisation design

A central composite design was generated using Design-Expert 9 software (Stat-Ease Inc., Minneapolis, US) to investigate the choice of sampling solvent, storage location, storage duration and extraction time as shown in Table 1. A face-centered CCD ( $\alpha=1$ ) with 5 replicates of each centre point was selected. This design was chosen as only three rather than five levels are required for each factor, and because it allowed the number of storage days at each level to be restricted to integer values. This resulted in a total of 78 experiments. Analysis of the data was conducted using Design-Expert 9, optimising the recovery of nitroglycerin, diphenylamine and ethyl centralite to a maximum. Two-way ANOVA was conducted to assess the significance of any main effects or two-way factor interactions on the recovery of each target compound, as measured by their GC–MS peak areas.

### 2.3. Sample preparation

48 in  $\times$  48 in  $\times$  0.019 in (1200 mm  $\times$  1200 mm  $\times$  0.48 mm) low carbon galvanised steel sheets were utilised as the recovery surface for all samples. Each sheet was cut into 12 in  $\times$  12 in (300 mm  $\times$  300 mm) plates, then further divided into 3 in  $\times$  3 in (75 mm  $\times$  75 mm) squares by scoring grid-lines into one side of each plate. The surface was cleaned using deionised water followed by ethanol and acetone, and allowed to completely dry at room temperature before use. Samples for each experiment were prepared by spiking 50  $\mu$ L of smokeless powder solution onto squares of the galvanised steel grid, and allowing the solvent to dry prior to sampling.

**Table 1**  
Factors and levels tested for face-centered central composite design.

	Levels
Swab Type	None (dry), acetone and isopropanol
Storage Location	Fume cupboard ( $\sim 25$ °C) and refrigerator ( $\sim 8$ °C)
Storage Duration	0, 3 and 6 days
Extraction Time	15, 37 and 60 min

## 2.4. Sample swabbing and extraction

Swabbing was carried out using Puritan sterile cotton-tip applicators. For wetted swabbing, the cotton-tips were briefly immersed in the desired solvent and the excess allowed to evaporate for 20 s. The cotton-tips were then rubbed back and forth across the sampling area for 10 s, ensuring adequate time to thoroughly sample the recovery surface area whilst minimising solvent evaporation, and the tips placed in 12 mL screw-top vials. Each vial was sealed using wax film, and placed in either a fume cupboard at room temperature or in a refrigerator for the required storage duration. For extraction, 5 mL of acetone was pipetted into each vial and the vial re-sealed using wax film. Vials were placed onto a WR Standard Analog Shaker Table on setting 3 for the desired extraction time. 60  $\mu$ L of the extract was transferred to a 20 mL SPME vial for analysis. This volume was determined based upon the properties of the solvent, as described in previous work [31].

## 2.5. Instrumental analysis

All analyses were conducted using a Thermo Trace Ultra GC equipped with a DSQ II MS and TriPlus Autosampler. Instrumental control, data acquisition and peak area integration was performed using Thermo Xcalibur software (v.2.0.7). The method utilised was adapted from that developed and optimised by Bors for DBSP analysis [31] in order to provide a shorter analysis time. Samples were incubated for 1 min at 60 °C, followed by a 5 min extraction onto a 100  $\mu$ m polydimethylsiloxane (PDMS) SPME fibre. After extraction, the fibre was desorbed in the GC inlet for 1 min in splitless mode. A PTV inlet ramp was used with an initial temperature of 200 °C for 0.25 min, ramped 10 °C s<sup>-1</sup> to 250 °C and held for 1 min. The fibre was conditioned offline at 240 °C for 5 min between each injection.

Separation was carried out on a Zebron ZB5-MS column (10 m  $\times$  0.18 mm  $\times$  0.18  $\mu$ m), using helium as the carrier gas with a flow rate of 1.5 mL min<sup>-1</sup>. The oven program was initiated at 40 °C held for 1 min, ramped at 40 °C min<sup>-1</sup> to 300 °C, and held for a further 1 min. The transfer line to the MS was held at 250 °C. Pulsed positive ion negative ion chemical ionisation (PPINICI) was used with a 200 °C ion source and methane reagent gas flow of 2 mL min<sup>-1</sup>. Selected ion monitoring (SIM) was used to detect nitroglycerin (m/z 42 and m/z 62 in negative mode, dwell time 25 ms), diphenylamine (m/z 170 in positive mode, dwell time 50 ms) and ethyl centralite (m/z 269 in positive mode, dwell time 100 ms). A typical chromatogram of a standard mixture is presented as Fig. S1 in the electronic supplementary information.

## 2.6. Pipe bomb trial

Assembly and detonation of the pipe bomb device was completed by the Indiana State Police Bomb Squad. A single device was constructed using PVC pipe (8 in  $\times$  1 in diameter: 200 mm  $\times$  25 mm) and endcaps (1 in diameter: 25 mm), with an approximately 50 g charge of Alliant Red Dot powder. The device was suspended by wire within a welded metal frame, with the end-caps pointing in the north and south directions. Six 12 in  $\times$  12 in (300 mm  $\times$  300 mm) galvanised steel plates were attached to each side of the frame (including above and below the device) by threading metal wire through holes drilled into the corners of each plate. A time fuse inserted through a hole in the south endcap was used to initiate the device. Following detonation, the steel plates were cut along the previously scored lines. The resulting segments were each given a unique alphanumeric identifier, and stored in individual polythene clip-seal bags prior to analysis. Sampling, storage and extraction were conducted using the optimal parameters determined by the central composite design.

## 3. Results and discussion

### 3.1. Preliminary considerations

To date, the majority of studies concerning the optimal recovery of explosive residues have utilised standard solutions of the target analytes, rather than 'real' residues generated through deflagration or detonation [13–19,21]. This is largely due to the difficulty in controlling these processes to obtain consistent deposition of residues [32], as well as the practicality and safety issues in conducting a large number of explosive experiments. It must be noted, though, that the use of standard solutions omits potential interferences caused by other components of the explosive material, such as plasticisers or surface modifiers. For this study, residues were thus simulated using a solution of the propellant rather than just the target analytes, in order to provide a more realistic representation of the post-blast residue composition. Unlike previous studies in which dichloromethane was utilised as the solvent for solution preparation and sample extraction, acetone was selected in this study due to its lower toxicity compared to dichloromethane, as well as its effectiveness in dissolving a wide range of explosive compounds [33]. Additionally, acetone can be applied to the direct extraction of PVC fragments, which would be dissolved by dichloromethane. A detonation trial employing the propellant in an explosive device was then conducted to test the developed recovery protocols on real residues, in addition to those simulated under controlled laboratory conditions.

Samples for the optimisation study needed to be prepared and analysed across multiple days, which could potentially result in extraneous variation. Such variations can typically be managed through blocking; wherein any 'nuisance' factors; i.e. those that have an effect on the response but are not of primary interest; are held constant whilst that of interest is permitted to vary [26,34]. In this manner, the effect of the factor of interest can be evaluated without interference of the nuisance factor. In this case, as the storage duration of the samples was a factor under investigation, it was not possible in this design to block for both the date of sample preparation and that of analysis. For practicality, it was decided to block samples according to their preparation date, with experiments in each block randomised in order to reduce any remaining nuisance effects as much as possible. Nevertheless, a degree of uncontrolled variation may still be present in the results.

### 3.2. Optimisation

A face-centered central composite design was used to optimise the response of the three target components to a maximum. Although results are presented for all three components, the primary goal was to determine suitable protocols for the recovery of nitroglycerin. As standard practice within most forensic laboratories, this component must be detected in order to report the presence of residues from double-base smokeless powder. Additional components such as diphenylamine and ethyl centralite may assist in identifying the brand of powder utilised, but these alone are not indicative of an explosive material.

Model fitting tests were used to assess the quality of the model for each component (Table 2). The coefficient of determination, R<sup>2</sup>, measures the percentage of response variation that can be explained by the model [35]. The R<sup>2</sup> was below 70% for nitroglycerin and diphenylamine, signifying that a large proportion of variation in the recovery of these components remains unexplained by the regression models. This variation is likely attributed to factors not included in the experimental design, such as the time interval between residue deposition and sampling. Additionally, low determination coefficients are frequently obtained when the response (i.e. peak area recovery) variation between individual

**Table 2**

Model fitting test results for response surface models constructed for nitroglycerin, diphenylamine and ethyl centralite based upon their GC-MS peak areas.

Model parameter	Nitroglycerin	Diphenylamine	Ethyl centralite
Model significance <i>p</i> -value	< 0.001	< 0.001	0.004
R <sup>2</sup>	55.3%	71.0%	40.1%
Lack-of-fit <i>p</i> -value	0.999	0.928	0.865

factor levels is small relative to the variation across the full factor range [26]. It is therefore possible that the low determination coefficients in this design are at least partially due to only small variations in recovery existing between particular factor levels.

Nonetheless, ANOVA found that the regression models for all three components were significant in modelling response variation ( $p < 0.005$ ) with no substantial lack of fit ( $p > 0.85$ ), indicating significant trends modelled within the dataset despite the low R<sup>2</sup> values. These models are therefore still valid in providing valuable information regarding the effect of the investigated factors on explosives recovery.

The optimum parameters and corresponding desirability for each individual component are shown in Table 3. The desirability is a measure of how suited the parameters are to producing an optimum response, with values ranging from 0 (least desirable) to 1 (most desirable). It can be seen that nitroglycerin and diphenylamine exhibit the same optimum parameters, with excellent desirability in both instances. The parameters for ethyl centralite, on the other hand, differ from the previous components and show a much lower desirability. This is likely due to the lower detection rate of ethyl centralite (82%), resulting from its low vapour pressure in comparison to nitroglycerin or diphenylamine (100% detection). The overall optimum parameters, while the same as those determined for nitroglycerin and diphenylamine, thus exhibit a decreased desirability due to the poor response expected from ethyl centralite. Regardless, as the desirability towards nitroglycerin was very high, these parameters were used for the remainder of the study.

Two-way ANOVA was used to evaluate the impact of each factor on the subsequent explosives recovery (Table 4). The choice of swabbing solvent was not identified as a critical factor for any of the three target components, possibly due to the similarity in recoveries obtained using acetone and isopropanol. The extraction time was also not found to be a substantial contributor. Recoveries of diphenylamine and ethyl centralite were substantially lower in samples stored at room temperature than those under refrigerated conditions ( $p < 0.001$ ). Conversely, storage temperature was found to have little impact on the recovery of nitroglycerin ( $p = 0.049$ ). It was expected that losses would occur at higher temperature due to residue evaporation, and that this would be most pronounced in the recovery of nitroglycerin due to its higher volatility than diphenylamine or ethyl centralite. The results obtained here instead

**Table 3**

CCD optimised parameters for the recovery of double-base smokeless powder components.

	Nitroglycerin	Diphenylamine	Ethyl centralite	Overall
Swab type	Isopropanol	Isopropanol	Dry	Isopropanol
Storage location	Fridge	Fridge	Fridge	Fridge
Storage duration	0 Days	0 Days	6 Days	0 Days
Extraction time	15 min	15 min	60 min	15 min
Desirability	1.000	0.996	0.672	0.777

**Table 4**

*p*-Values for all individual factors or interactions in the recovery of DBSP residues on steel.

	Nitroglycerin	Diphenylamine	Ethyl centralite
Sampling solvent	0.999	0.500	0.541
Storage location	0.049	< 0.001	< 0.001
Storage duration	0.292	< 0.001	0.003
Extraction time	0.627	0.391	0.327
Storage duration curvature	< 0.001	< 0.001	0.028
Extraction time curvature	0.925	0.472	0.695
Storage duration * Extraction time	0.058	0.012	0.176
Storage duration * Sampling solvent	0.964	0.478	0.408
Storage duration * Storage location	0.612	0.716	0.387
Extraction time * Sampling solvent	0.876	0.646	0.271
Extraction time * Storage location	0.838	0.865	0.788
Sampling solvent * Storage location	0.203	0.563	0.842

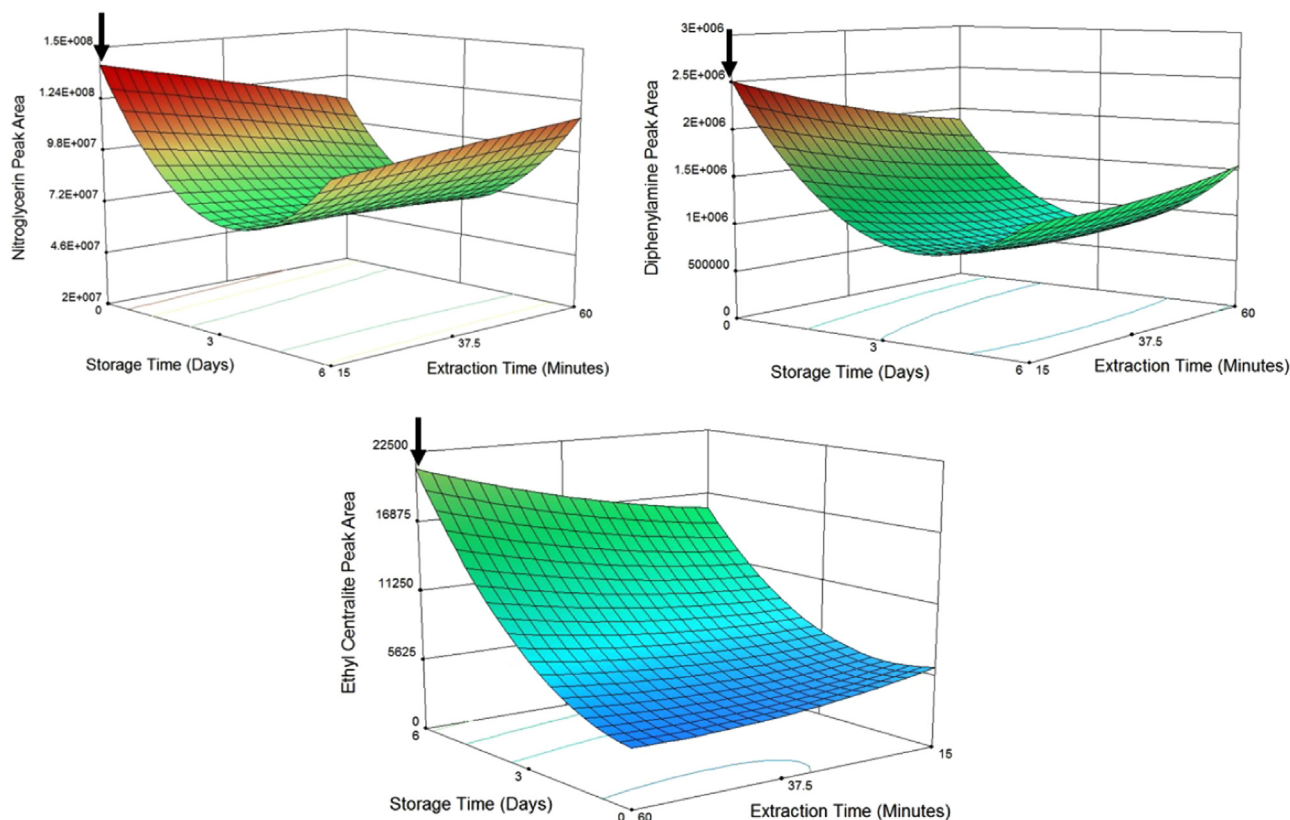
suggest that the decreased recoveries are more likely due to solvent evaporation from the swab material, resulting in increased binding of the residues as reported by DeTata et al. [13]. The greater recovery of nitroglycerin indicates that this component exhibits a lesser degree of binding to the swab material, allowing it to be more readily extracted when the swab is re-wetted.

Both diphenylamine and ethyl centralite were affected by the storage duration, with longer storage periods proving detrimental to the former ( $p < 0.001$ ) whilst appearing to improve recoveries of the latter ( $p = 0.003$ ). This is evident from the response surface plots (Fig. 1), which illustrate how recoveries of the components vary according to storage and extraction time. It can be seen that the anticipated response steadily increases with storage duration for ethyl centralite, whilst a minimum storage period produces the optimum recovery for diphenylamine. The former result was unexpected, as it was anticipated that a minimum delay between sampling and analysis would provide the highest explosive recovery. At present, there is insufficient evidence to speculate as to the cause of this result.

Interestingly, the response plot of both diphenylamine and nitroglycerin exhibit a substantial response curvature ( $p < 0.001$ ) associated with the storage duration of samples, in which those stored for 3 days exhibit much lower recoveries than those stored for 0 or 6 days. Although the initial decrease in recovery could be expected due to residue loss or decomposition while in storage, the increased recovery between three and six days of storage was not anticipated. It should be noted that due to the analysis of samples across multiple days, this curvature may be a result of block effects as previously discussed. Further work is hence required to determine whether the results obtained here can be reproduced, or are the result of extraneous variations in the data.

Interactions between the different factors were found not to have a significant impact on analyte recovery, with exception of the storage and extraction times. The combination of these factors was found to be influential on the recoveries of diphenylamine ( $p = 0.012$ ) and ethyl centralite ( $p = 0.028$ ), with longer extractions required for samples stored over 3 or 6 days than those analysed on the same day as preparation. These findings are again consistent with increased residue binding onto the swab material whilst in storage, resulting a longer period to extract the residues for analysis. This interaction also demonstrates the value of a central composite design, as univariate optimisation of the extraction time following three or six days of storage could produce a





**Fig. 1.** Response surface plots for the recovery of nitroglycerin and diphenylamine (isopropanol-wetted swabs) and ethyl centralite (dry swabs) stored under refrigerated conditions, as a function of extraction and storage time. Arrows indicate optimum points on each response surface.

false optimum extraction time of 60 min. By employing a CCD to model the entire response surface, it can be seen that the true optimum is in fact obtained when both the storage and extraction time are minimised.

### 3.3. Pipe bomb trial

As mentioned previously, the optimisation design was carried out using dissolved DBSP as a simulated residue matrix, in order to obtain reproducible deposits for sampling. However, actual residues generated through an explosive event are significantly more complex due to the changes that occur in the explosive as it reacts, degradation processes following reaction, and potential contamination from the local environment [36,37]. The optimised parameters were therefore tested on post-blast residues generated through a PVC pipe bomb detonation, in order to evaluate their applicability within an operational context.

Previous work by Bors et al. employed TV-SPME/GC-MS for the recovery of DBSP residues from steel pipe bomb device fragments

[31]. Although the device itself is a key source of post-blast residues, traces may also be recovered from “witness” materials surrounding the explosive charge [37]. This trial therefore aimed to recover residues on surfaces proximate to the device, rather than the device itself. Steel sheeting was chosen as the witness surface as it is a common non-porous material that could be expected to survive an explosive blast and accumulate post-blast residue that could be sampled using the techniques described above. Pre-cut steel sheets were attached to each side of a metal frame surrounding the device, which was suspended in the centre of the frame using metal wire. Following the explosion (Fig. 2), each plate was divided into 16 areas for sampling using the CCD-selected parameters. This resulted in excellent rates of detection associated with nitroglycerin (99.0%) and diphenylamine (95.8%), and moderate recovery of ethyl centralite (64.6%).

Relative peak area recoveries of the three target components from each witness plate are provided in Table 5. An example chromatogram is presented as Fig. S2 in the electronic supplementary information. The relative quantities of nitroglycerin



**Fig. 2.** Photographs of the PVC pipe bomb trial set-up, (a) prior to; (b) during; and (c) following initiation of the device.

**Table 5**

Relative GC-MS peak areas (normalised to maximum) of nitroglycerin, diphenylamine and ethyl centralite from galvanised steel witness plates following detonation of a PVC pipe bomb device. Values are averaged across 16 samples.

Plate Position	Nitroglycerin	Diphenylamine	Ethyl centralite
East	1.00	1.00	1.00
West	0.95	0.68	0.51
North	0.00	0.01	0.00
South	0.34	0.21	0.14
Top	0.54	0.33	0.78
Bottom	0.47	0.38	0.87

recovered from individual sections of each plate are also illustrated as a colour-coded heat map in Fig. 3. It can be seen that the highest overall recoveries were obtained from plates facing the sides of the device (east and west), rather than the end-caps. This is consistent with previous observations that the initial containment failure of PVC pipe bomb devices initiates in the pipe body, with the explosive plume primarily expanding from the sides of the device [38]. It should be noted that in pipe bombs constructed from steel, the first breach of the container has instead been observed to occur at the end-caps, which would presumably result in a differing distribution of post-blast residue on surrounding surfaces.

#### 4. Conclusions

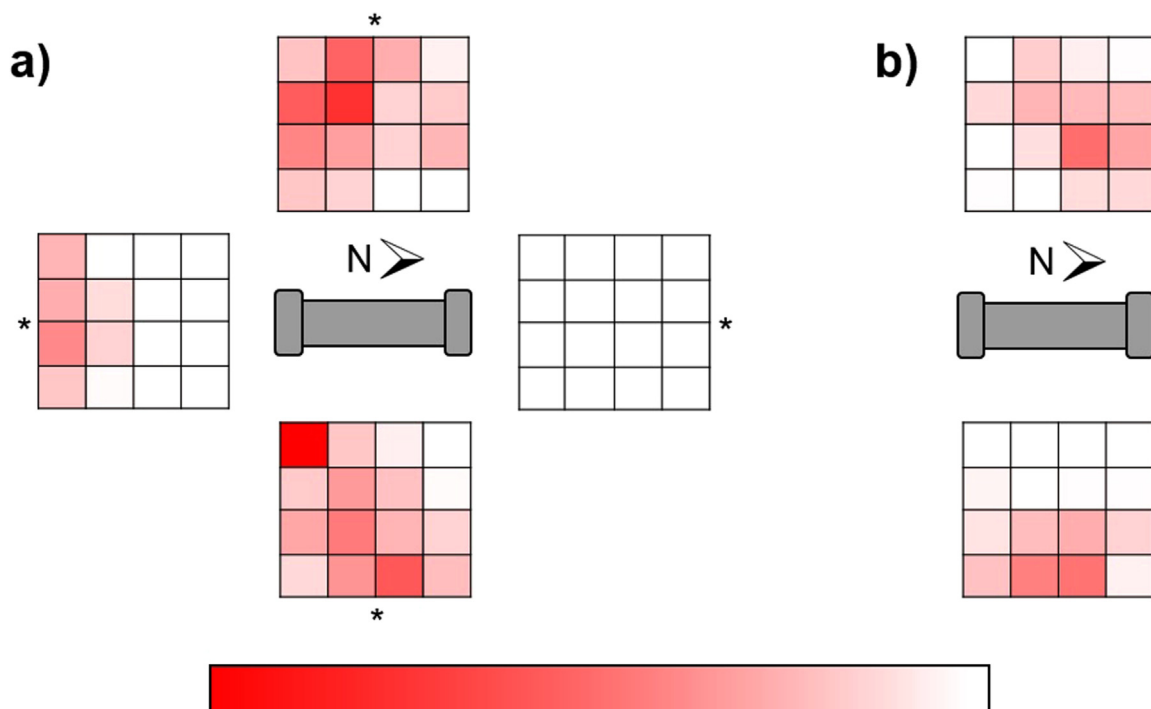
The use of a CCD in combination with TV-SPME GC/MS analysis was successfully used to develop statistically valid optimised protocols for the sampling, storage and extraction of double-base smokeless powder residues. Storage temperature was identified as the most important single factor, with recoveries of all three target components decreasing substantially when samples were not stored at low temperature. Varying recoveries were obtained with different swabbing solvents and extraction times, with isopropanol-wetted swabs extracted for 15 min giving the best

results. However, neither of these factors alone were determined as significant. Minimum storage durations were generally found to be ideal, with a substantial curvature in response also observed across the 0–6 day period tested, although this is potentially the result of block effects in the experimental design. As expected, longer storage durations also resulted in a longer extraction time required to desorb residues from the swabbing material. The presence of both curvature and factor correlations in the response surface also highlight the necessity of multivariate optimisation methods to detect and model higher-order interactions within complex datasets.

Application of the optimised parameters to real residues produced from a pipe bomb detonation resulted in successful recovery of all three target components, with nitroglycerin and diphenylamine each detected in over 95% of samples. The distribution of post-blast residues about the device was found to be higher on witness materials facing the sides of the device, consistent with the initial failure of PVC devices occurring in the pipe body. Future work may investigate the distribution of residues following detonation of steel-constructed devices, which have instead been observed to fracture at the end-caps.

It should be noted that although smokeless powder is widely used in the US, it is rarely encountered in countries such as Australia due to legal restrictions. In fact, of 41 powder-related explosive incidents reported to the Australian Federal Police between 2008 and January 2014, only seven were confirmed to involve smokeless formulations (G. Day, Australian Federal Police, personal communication, 2014). In these jurisdictions, explosive incidents are more likely to involve mining munitions or homemade peroxide explosives, such as TNT or TATP. Future work is thus required to determine optimum protocols for a wider range of explosives encountered in different geographical contexts.

The methodology presented in this study may also be applied to alternative forms of physical evidence. As with explosives analysis, the use of experimental design within a broader forensic context has been largely limited to the optimisation of instrumental analysis, rather than pre-analysis procedure such as



**Fig. 3.** Heat maps showing the distribution of nitroglycerin on witness plates (a) on each side; (b) above and below the PVC pipe bomb device. Colour scale is normalised against the highest nitroglycerin peak area. (\*) denotes the top edge of plates surrounding the device.

sample collection or storage. The use of multivariate optimisation methods will allow the development of scientifically rigorous evidential procedures across multiple forensic disciplines.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2016.04.048>.

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