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Research Paper

Quantification of smokeless powder (SLP) additives on hands after direct handling of bulk samples via a filter-and-shoot method

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ABSTRACT

Smokeless powders (SLPs) are easily available energetic materials that are often used in the construction of improvised explosive devices. Following a bombing incident, hand swabs are routinely collected from persons of interest (POIs) to assess potential SLP handling. However, the evidential significance of analytical findings remains difficult to assign due to the lack of systematic data on residue transfer. This study aimed to address this gap by determining the quantities transferred to hands (q_T) of three common SLP additives – diphenylamine (DPA), dibutyl phthalate (DBP), and ethyl centralite (EC) – following direct handling of bulk samples, with the specific goal of enabling the estimation of expected q_T ranges on a POI's hands under the hypothesis that they had handled SLP. A streamlined filter-and-shoot method was developed for residue collection and analysis, allowing direct chromatographic analysis without preconcentration steps. The results showed that q_T values typically ranged from the high nanogram to low microgram level, with DBP exhibiting the highest values and EC the lowest, mirroring their relative concentrations in the SLP formulations. The total mass of SLP handled (M_{SLP}) and the handler variability (H_{ID}) were identified as significant factors influencing q_T, whereas the type of SLP (T_{SLP}) had a much weaker effect. Notably, a strong linear dependence between q_T and M_{SLP} was observed for all the three compounds. Based on these findings, regression models were developed to estimate expected q_T ranges (including means and standard deviations) at different M_{SLP} values, providing a practical tool to refine interpretation where information on the amount of SLP handled is available. By establishing empirical data on SLP residue transfer, this study fills a critical knowledge gap in the literature, enhancing the ability to assess the significance of forensic findings and ultimately contributing to more robust interpretations in cases involving suspected SLP handling.

1. Introduction

Improvised explosive devices (IEDs) are a type of unconventional explosive weapon incorporating energetic materials that are readily available commercially and/or are manufactured from accessible precursors [1]. Because of this, they can be easily prepared in homemade settings and used in different criminal activities, including terrorist attacks and volume crimes, such as ATM thefts and blast fishing. Action on Armed Violence estimated that IEDs were accountable for 36 % of all the explosive weapon uses recorded globally in the period between 2010 and 2022 (14,242 cases), as well as responsible for 49 % of the related civilian casualties (147,482 victims) [2]. Therefore, the possibility to determine whether a person of interest (POI) handled an IED at the time of the crime is crucial for law enforcement authorities in the aftermath of a bombing event [3].

The energetic materials used in IEDs are diverse and include military, commercial and homemade explosives. Amongst these, smokeless powders (SLPs) are particularly prevalent, especially in the

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manufacturing of pipe bombs [4,5], as they are commonly used as propellants in firearm cartridges, making them safe to handle, relatively inexpensive and easily accessible from gun shops. SLPs are nitrocellulose-based explosives that, depending on the formulation, may contain various other organic additives, including energetic compounds (e.g., nitroglycerin), stabilisers (e.g., diphenylamine and ethyl centralite) and plasticisers (e.g., dibutyl phthalate) [6,7]. Testing a POI for explosive handling typically begins with the collection of hand samples [8]. Standard protocols commonly involve the use of swabs or wipes soaked in lowly toxic, alcohol-based solutions, followed by their back-extraction and, eventually, pre-concentration/purification using techniques such as solid phase extraction (SPE) [8–12]. The extracted residues are then analysed using chromatographic methods. Ion chromatography (IC) and capillary electrophoresis (CE) are the typical methods of choice for the analysis of inorganic explosive-related components, while gas chromatography (GC) and liquid chromatography (LC) are preferred for the analysis of the organic explosive-related components [13–15]. Increasingly, all these techniques are coupled with mass spectrometry (MS) to enhance analytical sensitivity and selectivity, as well as to enable retrospective data analysis [16].

Beyond analytical detection, answering the question "did the POI handle an explosive at the time of the crime?" is a complex inferential procedure that requires weighing findings against case-specific expectations. Assigning evidential values to such findings through likelihood ratios is widely recognised as the most logically coherent framework for evidential assessment in forensic science [17,18], and broadly applicable models have been developed to support interpretation at the activity level [19]. However, the effectiveness of this approach in explosive handling cases depends critically on the ability to estimate the quantities of explosive residues that would be expected on the POI's hands if they had handled an energetic material, as well as the levels that could arise from background contamination [20]. These estimations, in turn, require robust empirical data regarding the transfer, persistence, and prevalence of explosive-related species [19]. Focusing specifically on the primary transfer, Twibell *et al.* [21] were the first back in the 80's to quantify nitroglycerin (NG) in hand swabs after the handling of blasting gelatine. Using GC-ECD, they reported quantities ranging from nanogram levels for well-wrapped cartridges, to microgram and milligram levels for poorly wrapped cartridges and raw material, respectively. The same authors later investigated the transfer of trinitrotoluene (TNT), cyclonite (RDX) and pentaerythritol tetranitrate (PETN) after direct contact with military explosives [22]. They observed quantities in the microgram range for all three compounds, as well as systematic variations that were apparently linked to the chemistry of the compound. Indeed, the highest values were generally observed for RDX and the lowest for TNT. All these findings were more recently corroborated by Perret *et al.* [23] using LC-MS/MS, who repeated some of the experiments proposed by Twibell *et al.* and also carried out additional tests with new explosive formulations containing the same chemicals. This included dynamite, cutting charges and detonating cords. Regarding inorganic explosives, Gallidabino *et al.* [24] investigated the transfer of benzoate, nitrate and perchlorate during the handling of black powder using IC-HRMS. They reported quantities transferred in the microgram range.

All these studies provided valuable insights into the primary transfer of explosives and identified some influential factors. However, they were sporadic and lacked a systematic approach. For instance, the impact of the amount of explosive handled was never thoroughly assessed, nor was the additional variability potentially introduced by differences in explosive types and individual handlers. Moreover, most research has focused on species associated with high-order explosives, whereas species associated with low-order explosives, which are more commonly used in IEDs, have remained largely under-investigated. Therefore, this work aimed to address these knowledge gaps by determining the quantities transferred to hands (q_T) of three common SLP additives – namely, diphenylamine (DPA), dibutyl phthalate (DBP) and ethyl centralite (EC) – following direct handling of bulk samples, with the specific goal of providing essential data to support the estimation of expected q_T ranges on a POI's hands under the hypothesis that they had handled SLP. To achieve this, a streamlined filter-and-shoot method was first developed for SLP residue collection and analysis, incorporating wet swab sampling and allowing direct chromatographic analysis without preconcentration steps. GC–MS and LC-MS/MS were compared as potential determination methods to ensure optimal analytical performance. Then, four volunteers were asked to handle bulk samples, and their hands sampled. The effect of the total mass of SLP handled (M_{SLP}) on the q_T values was specifically investigated, while also varying the type of SLP handled (T_{SLP}), and the handler itself (H_{ID}) to assess the additional variability introduced into the data. Where possible, results were modelled using computational methods and analysed statistically to identify trends and/or transfer characteristics that could refine the estimation of expected q_T ranges in forensic casework.

To the best of the authors' knowledge, this is the most extensive systematic study conducted to date on the primary transfer of explosive-related species on hands after direct handling of bulk samples. It is also the first study to systematically control key factors of forensic relevance (i.e., M_{SLP}, T_{SLP} and H_{ID}) to rigorously assess their impact on residue transfer.

2. Experimental

2.1. Chemicals and materials

Water was purchased from Thermo Fisher Scientific (Loughborough, UK), methanol (MeOH) and ethanol (EtOH) were purchased from Sigma-Aldrich (Dorset, UK). All these solvents were of HPLC grade (>99.9 %). Ammonium acetate (>99.9 %) was also obtained from Sigma Aldrich. Cotton balls used for swabbing were purchased from Sainsbury's (London, UK) and plastic syringes were purchased from Medicina (Bolton, UK).

Standard reference materials of seven compounds previously identified in SLPs were obtained from different chemical companies. These were (in alphabetical order): akardite 2 (AK2; Sigma Aldrich, 95 %, CAS: 13114–72-2), dibutyl phthalate (DBP; Sigma Aldrich, 99 %, CAS: 84–74-2), diphenylamine (DPA; Thermo Fisher Scientific, 98 %, CAS: 122–39-4), ethyl centralite (EC; Sigma Aldrich, 97 %, CAS: 85–98-3), methyl centralite (MC; AMBeed, 95 %, CAS: 611–92-7), 4-nitrodiphenylamine (4NDPA; Thermo Fisher Scientific, 98 %, CAS: 836–30-6) and nitrosodiphenylamine (NNDPA; Sigma Aldrich, 98 %, CAS: 93951–95-2). For each substance, an individual stock solution was prepared at a concentration of 1000 mg L^{-1} in MeOH. Stock solutions were stored in the dark (freezer) at −20 °C. Working solutions were freshly prepared daily by dilutions of stock solutions using different solvents depending on the experiment.

2.2. GC–MS equipment and conditions

Although both GC–MS and LC-MS/MS were initially evaluated for analytical performance, only GC–MS was used for quantification in this study. The detailed LC-MS/MS conditions are provided in the Supporting Information. The GC–MS system consisted of an Agilent 7890A gas chromatograph (Agilent Technologies, Stockport, UK), coupled to an Agilent 5975C mass spectrometer, and equipped with an Agilent 7683 autosampler.

Separation was carried out on a HP1 column (25 m × 0.2 mm × 0.11 μm) from Agilent using a temperature-programmed method. The carrier gas was helium and column flow maintained at 1.2 mL min^{-1}. Injection was carried out in splitless mode for 1.5 min and the injection volume was set to 1 μL. The oven ramp was programmed as follows: 80 °C for 1 min, increased to 180 °C at 20 °C min^{-1}, increased to 210 °C at 5°C min^{-1}, increased to 280 °C at 20 °C min^{-1} and held for 1 min (total run time: 16.5 min). An initial temperature of 80 °C was particularly

Table 1
Main characteristics of the ammunition purchased for this study, including the measured concentrations (m/m) of the main additives in the corresponding smokeless powders (SLPs).

Abbr.	Brand	Bullet mass [gr][a]	Bullet type[b]	SLP grain shape	Additive concentration (m/m) in SLP [mg g^{-1}]		
					DPA	DBP	EC
PPU	Prvi Partizan	55	JSP	Disc flake	11.9	78.9	0.4
WIN	Winchester	55	Silvertip	Disc flake	8.2	54.6	6.1
FED	Federal	55	JSP	Disc flake	7.4	51.6	2.4
				MEAN	*9.2*	*61.7*	*3.0*

[a] Bullet masses are given in grains (1 gr = 64.80 mg).
[b] JSP: jacket soft point.

selected to avoid peak splitting during the analysis of alcoholic extracts [25]. After separation, the column flow was increased at 3.0 mL min^{-1} and the column temperature to 310 °C for 5 min for post-run conditioning. The transfer line between the column and the MS was held at 280 °C. Ionisation was carried out through electron impact (EI) and selected ion monitoring (SIM) was used (see Table S1 for a list of targeted ions). Solvent delay was set to 4.5 min, and MS source and quadrupole temperatures were set to 230 °C and 150 °C, respectively. No carryovers were observed. A quality control solution at a concentration of 10 mg L^{-1} was injected every five samples.

2.3. Analytical performance evaluation

Limits of detection (LODs), limits of quantification (LOQs), linearity and repeatability were assessed on both instruments following the ICH guidelines [26]. Linearity was studied on a series of solutions spiked at ten different concentrations between 0.01 and 10 mg L^{-1}, which were analysed in triplicate. In particular, the coefficients of determination (R^2) were calculated on log-transformed data. LODs and LOQs were estimated from the linear calibration curves and were respectively defined as 3 and 10 times the estimated standard deviations of peak areas divided by the slope. Repeatability was assessed on a series of solutions spiked at three different concentrations (i.e., 0.1 mg L^{-1}, 1 mg L^{-1} and 10 mg L^{-1}), which were injected six times. The relative standard deviations (RSD) were calculated on the observed peak areas.

2.4. Analysis of SLPs

The SLPs used in this study were directly recovered from live ammunition. Three ammunition boxes were purchased from various gun shops. All of them were of .223 Remington calibre, but from different brands. The three ammunition types were: (1) Prvi Partizan (PPU), (2) Winchester (WIN) and (3) Federal (FED) (see Table 1 for a full list of characteristics).

From each ammunition box, two cartridges were opened using a kinetic hammer, the respective SLPs collected and homogenised. Samples from each of the SLPs were extracted and preliminary analysed following an extraction procedure previously reported by Kesic *et al.* [25]. Briefly, 20 mg were weighed and transferred into a 15 mL glass centrifuge tube (Thermo Scientific), where 2 mL of MeOH were added. The tube was vortexed for 10 s, ultrasonicated for 15 min and then vortexed again for 10 s, before being centrifuged for 5 min at 2000 rpm. The supernatant was finally transferred to a 2 mL vial and analysed with the GC–MS method. For quantification, 10-fold and 100-fold dilutions were prepared to bring analyte concentrations within the range of the calibration curve. Results are reported in Table 1. Although other minor additives were observed, DPA, DBP and EC were the only compounds detected at a concentration $\geq$1 mg g^{-1} in at least one SLP and, therefore, the only ones selected for this study.

2.5. Handling experiments

The handling experiments were conducted following a protocol adapted from previous works [23,24]. Briefly, volunteers were first required to thoroughly wash their hands twice: first with soap and tap water, and then with tap water alone to remove any soap residue. They were then instructed to rub pre-weighted bulk samples of SLP between their palms for 30 s, while minimising particle loss. Finally, they were asked to clap their hands multiple times to dislodge any loose particles before proceeding with the sample collection.

Four volunteers participated in the primary transfer experiments. To assess the effect of the mass of SLP handled, four different masses were tested: 100 mg, 500 mg, 1000 mg, and 2000 mg (with 2000 mg set as the upper limit for health and safety reasons). One participant (P1) handled samples from all three available SLP types, while the remaining three participants (P2–P4) each handled only one specific SLP type (P2 → PPU; P3 → WIN; P4 → FED). Each experiment was performed in duplicate, resulting in a total of 48 samples collected. Additionally, a procedural blank was taken before each handling session by swabbing

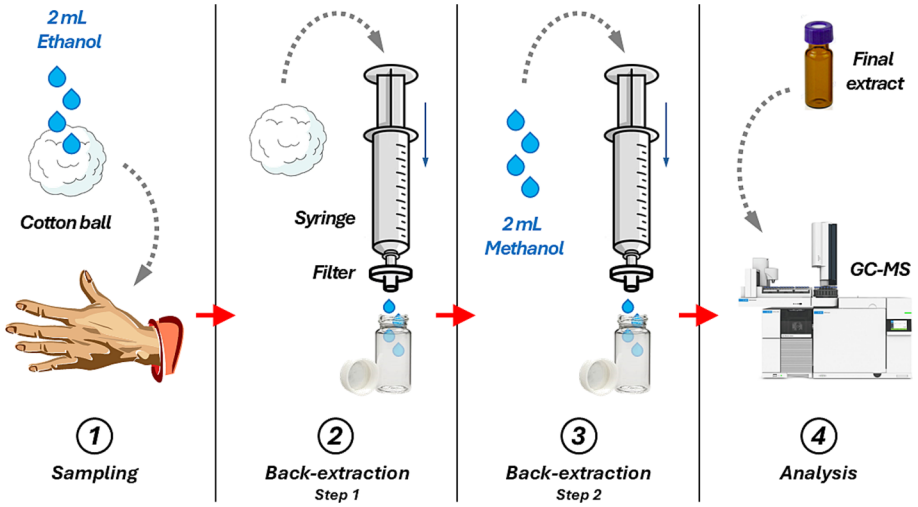


Fig. 1. Visual representation of the sample preparation procedure used in this work. The procedure consisted of four main steps: (1) hand sampling using a moistened cotton ball, (2) transfer of the cotton ball into a syringe followed by a first back-extraction through compression, (3) addition of 2 mL of methanol and a second back-extraction by compression, and (4) analysis of the final extract using GC–MS.

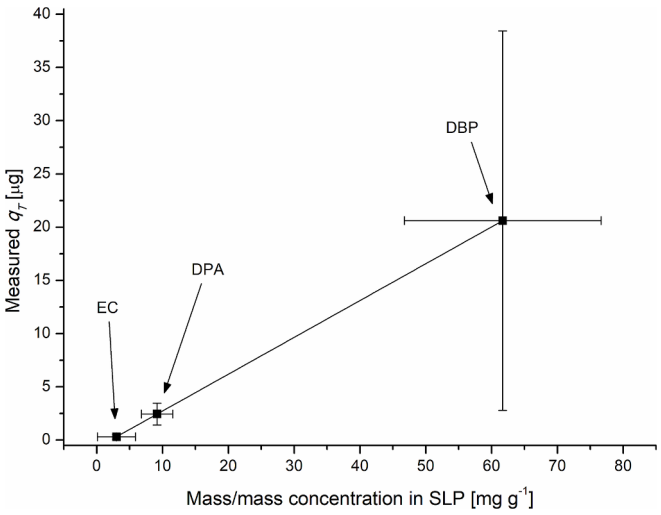


Fig. 2. Quantities of additives transferred to hands (q_T) plotted against their initial concentrations in the SLP. The solid line represents the mean trendline derived from a linear–linear regression model. Data shown correspond to an SLP handling mass of 1000 mg (M_{SLP} = 1000 mg), with similar trends observed for other M_{SLP} values tested. Error bars represent standard deviations: on the y-axis, they reflect variability in q_T values (n = 12); on the x-axis, they reflect variability in the initial concentration measurements (n = 3, one per SLP). Additional plots for the other M_{SLP} conditions (100, 500, and 2000 mg), including all individual data points, are provided in the Supporting Information (Fig. S4).

the participant's hands.

2.6. Sample collection and preparation

A visual representation of the procedure is provided in Fig. 1. Swabs were prepared by cutting cotton balls in half and soaking each half with 2 mL of EtOH. For sampling, a single soaked swab was used to thoroughly rub both hands of the participant, focusing on the palms, fingers, and spaces between fingers to ensure comprehensive coverage of all areas potentially in contact with the SLP sample. The swab was then placed in a 20 mL plastic syringe barrel and compressed with the plunger to back-extract the collected residues. The initial extract was collected in a 21.25 mL glass vial. Subsequently, the plunger was removed, and 2 mL of MeOH was added onto the swab, which was then squeezed again to enhance residue recovery. MeOH was specifically chosen for this second extraction step to lower the boiling point of the final extract, facilitating its compatibility with GC–MS. The second fraction was combined with the first one, and the total volume adjusted to 4 mL with additional MeOH. This final extract was vortexed for 20 s and an aliquot transferred into a 2 mL amber glass vial for GC–MS analysis. A two-point calibration approach was used for quantification.

Back-extraction yields were evaluated by spiking eight moistened swabs with 40 µg of each target additive and comparing the resulting peak areas with those obtained from the analysis of a 10 mg L^{-1} standard solution. Spiking of participant's hands was not feasible for health and safety reasons. Therefore, collection efficiencies from hands were estimated by asking five volunteers to handle 2 g of the WIN SLP and performing up to five consecutive samplings of their hands. Values were calculated by comparing the peak areas observed in the first iteration with the cumulative total [27].

2.7. Data analysis

The quantities of additives recovered from hands (q_R) were first determined by multiplying the measured concentrations by the final extract volume (4 mL). Since back-extraction yields were confirmed to be 100 % (Fig. S2), no further corrections were necessary at this stage. Following established analytical determination practices [28,29], the q_T values were then calculated by adjusting the q_R values based on the observed average collection efficiency, which was determined to be approximately 30 % (Fig. S3). Finally, the transfer efficiencies (f_T) were calculated by dividing the q_T values by the corresponding amounts of additives handled, as described by the following equation:

$$f_T = q_T/(M_{SLP} \times C) \quad (1)$$

where M_{SLP} is the total mass of SLP handled and C is the measured concentration of the related additive in the SLP (Table 1).

The effects of the three controlled variables (M_{SLP}, T_{SLP} and H_{ID}) on q_T were initially assessed visually using data plots. A three-factor analysis of covariance (ANCOVA) was then performed to further support the conclusions drawn from this initial exploration. This method was selected over a standard analysis of variance (ANOVA) due to the combination of continuous (M_{SLP}) and discrete (T_{SLP} and H_{ID}) variables [30]. The significance of the effects was evaluated using the F-test p-values, while size effects were measured using partial η^2 (eta-squared). Given the unbalanced design of the dataset, Type III (partial) sums of squares were used in all calculations, as they are more appropriate than Type I or Type II in such contexts [31]. Residual analysis indicated moderate deviations from normality and homogeneity of variances. As noted by Keselman *et al.* [32], ANCOVA can be sensitive to such assumption violations, potentially leading to inflated false positive rates. However, no suitable parametric or non-parametric alternatives exist for multi-factor models of this complexity. In this context, the combination of ANCOVA with Type III sums of squares, while not correcting for assumption violations, was considered the most appropriate available strategy. Type III sums of squares, in particular, allow for the estimation of each effect while adjusting for all other model terms, thereby helping to mitigate the risk of biased results [31].

Regression analysis was applied to further evaluate the relationships between q_T and M_{SLP}, as well as f_T and M_{SLP}. Several models were fitted to the data considering different combinations of log-transformed variables, including linear–linear, linear-log, log-linear and log–log transformations [33]. Since residual analysis indicated a slight increase in the variance as a function of M_{SLP}, heteroscedasticity was accounted for using a weighted least squares regression approach. The weights were derived from an auxiliary variance model, where variance was assumed to be proportional to M_{SLP} [34]. This model was of the form $\sigma^2 = c \times M_{SLP}$, where σ^2 represents the estimated variance and c is a regression coefficient.

2.8. Software

Chromatograms for GC–MS analyses were analysed using Agilent ChemStation v. E.01.00.237, and those for LC-MS/MS using Thermo XCalibur v. 2.0.7. This software was also used for the respective peak area extraction. R statistical computing software v. 4.4.1 [35] was used for most of the subsequent data analysis. In particular, the following packages were adopted: "*stats*" [35] for linear regression analysis (included log-linear, linear-log and log–log models) and ANCOVA modelling, and "*effectsize*" [36] for ANCOVA result analysis and partial η^2 calculations.

3. Results and discussion

3.1. Preliminary method development

GC–MS and LC-MS/MS have previously been shown to offer distinct advantages for the analysis of SLP compounds [15]. Therefore, both techniques were tested on a selection of seven additives commonly found in SLP formulations, and two targeted methods were optimised on available instruments. Their respective analytical performances are

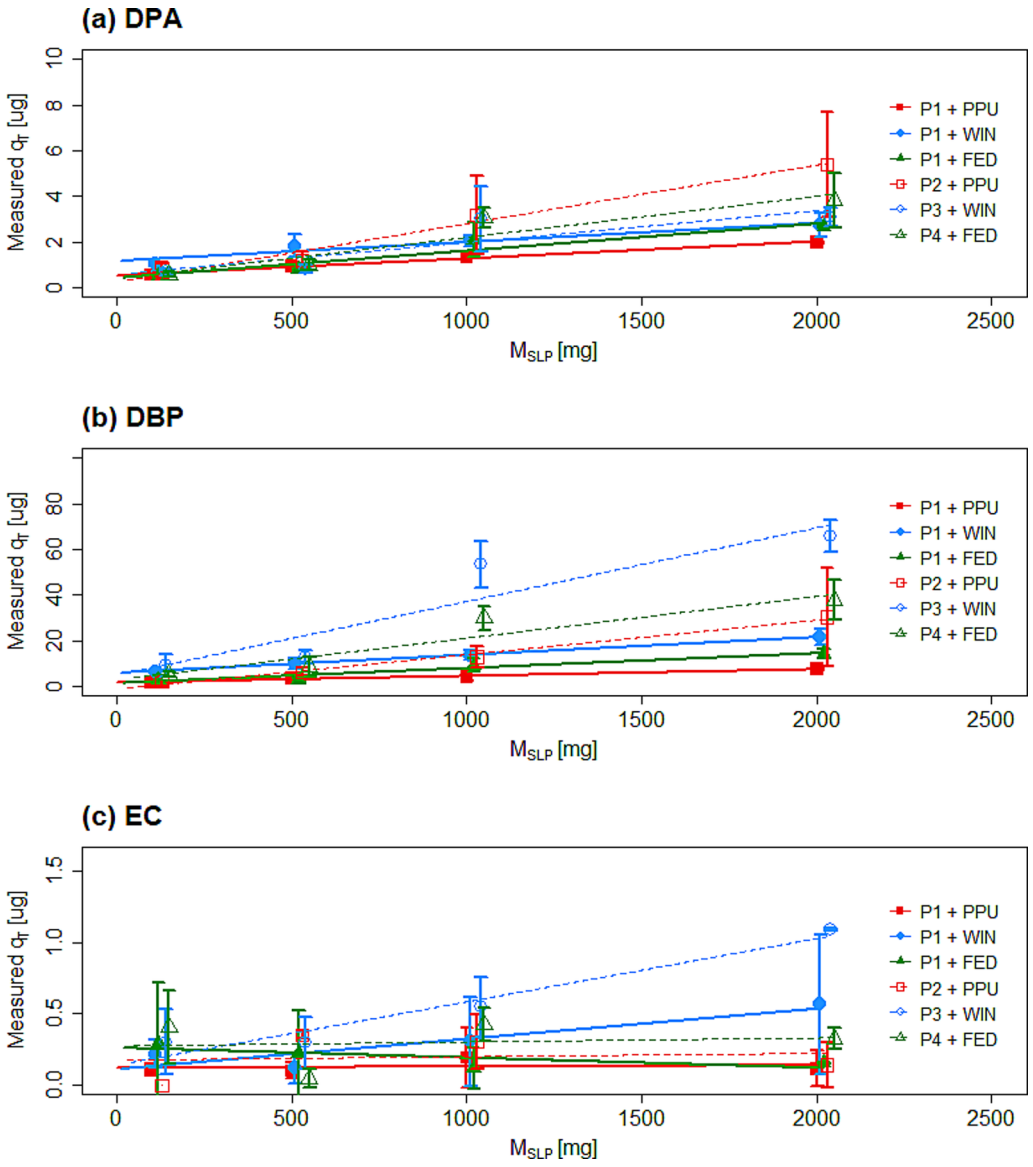


Fig. 3. Quantities of additives transferred to hands (q_T) plotted against the total mass of SLP handled (M_{SLP}) for each combination of handler (H_{ID}) and SLP type (T_{SLP}) tested in this study. Error bars represent the standard deviations of the measured values. The solid lines represent the mean trendlines, highlighting variations in residue transfer across the different situations. These trendlines were derived from linear-linear regression models, which were identified as the best fit among those tested (see Table S4). The datasets are offset by M_{SLP} = 10 mg for clarity.

Table 2
Summary statistics of the collected data, grouped by mass of SLP handled (M_{SLP}). For each M_{SLP} value, the mean and standard deviation (SD) are reported for the measured quantities of additives transferred to hands (q_T) and the corresponding transfer efficiencies (f_T). Each group consist of n = 12 samples, for a total sample size of n_{tot} = 48. Predicted q_T values, derived from the regression models in Table 4, are also included for comparison.

M_{SLP} [mg]		DPA			DBP			EC		
		q_T [µg]		f_T [ppm][a]	q_T [µg]		f_T [ppm]	q_T [µg]		f_T [ppm]
		Measured	Predicted		Measured	Predicted		Measured	Predicted	
100	Mean	0.692	0.686	784	4.725	4.496	842	0.223	0.215	1040
	SD	0.229	0.271	291	3.252	4.041	626	0.218	0.123	1122
500	Mean	1.105	1.285	250	7.365	10.031	255	0.189	0.248	400
	SD	0.427	0.606	109	4.167	9.036	165	0.162	0.275	586
1000	Mean	2.452	2.033	282	20.612	16.950	368	0.317	0.290	248
	SD	1.022	0.857	127	17.816	12.778	339	0.212	0.389	316
2000	Mean	3.285	3.530	184	29.580	30.789	258	0.399	0.374	88
	SD	1.395	1.212	69	21.126	18.071	196	0.395	0.550	85

[a] f_T values are reported in parts per million (1 % = 10,000 ppm).

Table 3
Summary of the three-factor ANCOVA results examining the influence of the total mass of SLP handled (M_{SLP}), the type of SLP handled (T_{SLP}) and the handler itself (H_{ID}) on the quantities of additives transferred to hands (q_T). *p*-Values from *F*-test were used to determine the significance of each effect, i.e., whether any observed variation in the q_T values was due to chance. The lower the *p*-value, the more likely the variation was not due to chance. Partial η^2 (eta squared) were calculated to examine the effect size, i.e., the relative magnitude of any observed variation in the q_T values (measured in terms of proportion of variance explained). The larger the partial η^2, the greater the influence the parameter has. Full results are reported in Table S3.

Factor	DPA		DBP		EC	
	p-value	Partial η^2	*p*-value	Partial η^2	*p*-value	Partial η^2
M_{SLP}	< 0.001 (***)[a]	0.63	< 0.001 (***)	0.53	0.026 (*)	0.11
T_{SLP}	0.237 ()	0.07	0.213 ()	0.07	0.321 ()	0.05
H_{ID}	0.007 (**)	0.25	< 0.001 (***)	0.42	0.121 ()	0.13

[a] Significance codes: (***) < 0.001, (**) < 0.01, (*) < 0.05, (.) < 0.1, () < 1.

compared in Table S2. While LC-MS/MS achieved lower LODs for the most thermolabile probes (i.e., 4NDPA and NNDPA), GC–MS demonstrated superior overall performance for the main additives targeted in this study (i.e., DPA, DBP and EC) and, in particular, better repeatability at low concentrations. For example, the RSD for DPA at 0.1 mg L^{-1} was 8.1 % with GC–MS, compared to 81.5 % with LC-MS/MS, with similar trends for EC and DBP. Consequently, GC–MS was selected for further method development (Fig. S1).

A wet swabbing approach using cotton balls was selected for hand sampling, in line with established field practices [3]. To streamline the process, however, here the approach was adapted into a filter-and-shoot procedure that involved moistening the cotton balls with just 2 mL of EtOH, followed by back-extraction with an additional 2 mL of MeOH in a 20 mL plastic syringe, and direct injection of the resulting extracts into GC–MS (Fig. 1). Back-extraction yields were estimated at 100 % (Fig. S2). Therefore, compared to conventional sample preparation methods which typically require at least 10 mL of solvent [24,37], this modified approach reduced solvent consumption by over 50 % without compromising the back-extraction efficiency. Additionally, it enhanced concentration factors to levels comparable to those achieved with SPE [38,39], effectively enabling direct chromatographic analysis without the need for preconcentration steps.

Collection efficiencies from hands were determined to be approximately 30 % (Fig. S3). Although no direct comparisons could be made due to the lack of prior studies on hand sampling, these values align with previous research using cotton balls to recover explosive residues from challenging surfaces such as plastic [8,40]. Overall, the final method offered enhanced throughput compared to other published alternatives and was deemed suitable for the purpose of this study. Notably, purely alcohol-based solvents were used instead of alcohol:H_2O mixtures to avoid water in the extracts and ensure GC–MS compatibility. This choice was only viable because no water-soluble species (e.g., ions) were targeted.

3.2. General trends in the measured quantities

Four volunteers (hereafter referred to as H_{ID} = P1–P4) participated in the handling experiments. Using the developed method, the quantities of DPA, DBP and EC recovered from their hands (q_R) were first measured and then adjusted for the average collection efficiency (i.e., 30 %) to estimate the actual quantities transferred (q_T). This adjustment ensured that the data were method-independent. Additionally, the total mass of SLP handled (M_{SLP}) and the type of SLP handled (T_{SLP}) were systematically varied across the experiments to assess their influence on residue transfer.

On average, the measured q_R values were 0.565 ± 0.409 (SD) μg for DPA, 4.671 ± 5.101 (SD) μg for DBP and 0.085 ± 0.080 (SD) μg for EC. After adjusting for collection efficiency, the estimated q_T values were 1.883 ± 1.362 (SD) μg for DPA, 15.571 ± 17.003 (SD) μg for DBP and 0.282 ± 0.267 (SD) μg for EC. Therefore, the results indicated that the quantities transferred typically ranged from the high nanogram to low microgram range, with DBP consistently showing the highest values and EC the lowest. The latter trend closely mirrored the initial concentrations of the additives in the SLPs (Fig. 2; see also Fig. S4), suggesting a positive relationship between quantities transferred and additive content.

The q_T values were consistently five to seven orders of magnitude lower than M_{SLP}, confirming that only trace amounts, at the parts-per-million (ppm) level, are transferred during handling. Despite these low levels, the results align well with previous transfer studies on other explosive-related species, which have also reported values within the nanogram-to-microgram range [21–24]. In contrast, comparisons with background levels remains challenging, due to the scarcity of relevant quantitative data published in the literature. The only study that specifically determined background levels of DPA and EC on hands reported no quantifiable amounts of these compounds [41], while no equivalent data exist at all for DBP. As an internal reference, no measurable levels of the target additives were detected in procedural blank samples in this work.

3.3. Analysis of factor effects

A high degree of variability was observed in the measurements, as reflected by the large standard deviations. To investigate whether this variability could be attributed to any of the controlled variables, the q_T values were initially plotted against M_{SLP} for the different combinations of T_{SLP} and H_{ID} and visually inspected (Fig. 3). In most cases, q_T increased proportionally with M_{SLP}, perhaps as expected, confirming that handling larger masses of SLP typically resulted in greater residue transfer to hands and, consequently, higher detected quantities of additives. This trend was consistent across all scenarios for DPA and DBP, whereas EC exhibited more irregular trends likely due to its lower overall levels which increased measurement uncertainty and made it more challenging to discern clear patterns.

Among the other controlled variables, H_{ID} appeared to have a stronger influence on q_T than T_{SLP}. This was particularly evident when analysing data from P1, the only participant who handled all three SLP types. Indeed, the differences observed across T_{SLP} for P1 were much smaller compared to the differences across H_{ID} for the different SLP types (Fig. 3), suggesting that inter-individual variability played a more substantial role in q_T variation than formulation differences. Interestingly, further examination of data from P1 also indicated that, for the single additives, a higher concentration in the SLP formulation does not automatically result in a larger quantity transferred to hands. For instance, while PPU contained the highest concentration of DPA and WIN the lowest, their respective q_T values tended to follow the opposite pattern. This discrepancy suggests that factors beyond the additive concentration – such as the flake size or surface properties – may also influence transfer efficiency, leading to unpredictable variations in q_T that cannot be solely attributed to composition differences.

To statistically confirm these observations, an analysis of covariance (ANCOVA) was conducted. The results largely supported the initial visual assessment (Table 3). In particular, M_{SLP} emerged as the strongest determinant of q_T, showing a very highly significant effect on DPA ($p < 0.001$, partial $\eta^2 = 0.63$) and DBP ($p < 0.001$, partial $\eta^2 = 0.53$), while its effect on EC remained significant ($p = 0.026$, partial $\eta^2 = 0.11$). H_{ID} was the next most influential factor, exerting a highly significant effect on DPA ($p = 0.007$, partial $\eta^2 = 0.25$) and a very highly significant effect on DBP ($p < 0.001$, partial $\eta^2 = 0.42$), whereas its effect on EC was not significant ($p = 0.121$, partial $\eta^2 = 0.13$). These results further reinforce the strong influence of inter-individual variability in residue transfer,

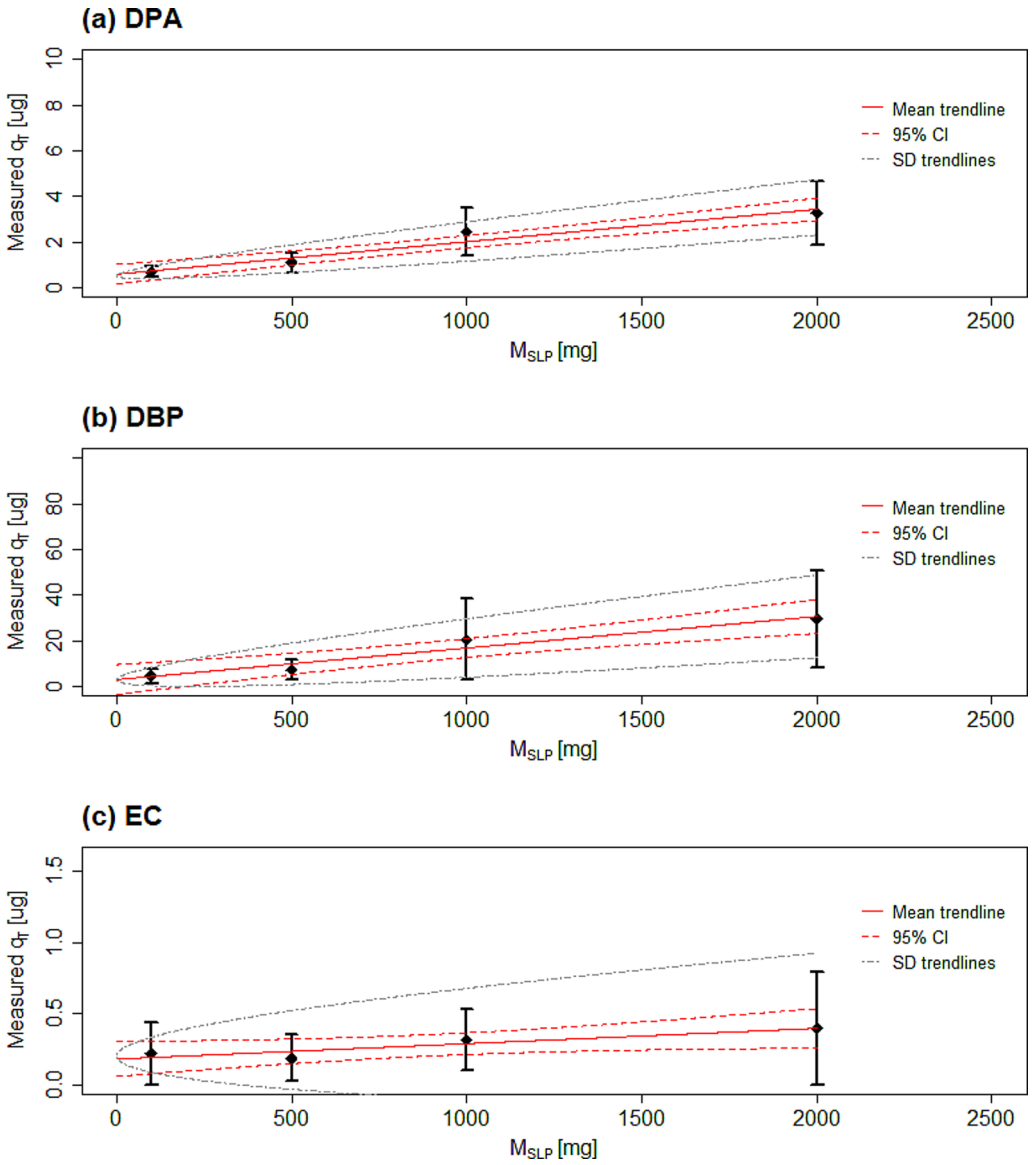


Fig. 4. Quantities of additives transferred to hands (q_T) plotted against the total mass of SLP handled (M_{SLP}) after pooling data across the different combinations of handler (H_{ID}) and SLP type (T_{SLP}). Error bars represent the standard deviations of the measured values. The solid red lines represent the mean trendlines, while the dashed red lines indicate the respective 95 % confidence intervals (CIs). The gray dotted lines correspond to the standard deviations (SD) trendlines. All these trendlines were derived from the linear–linear regression models reported in Table 4.

Table 4
Regression models derived from data pooled across the different combinations of handler (H_{ID}) and SLP type (T_{SLP}), providing estimates for the expected mean (μ_q) and variance (σ_q^2) of q_T as a function of M_{SLP}. Due to the presence of heteroscedasticity, where the spread of the q_T values increased with increasing M_{SLP}, the variance was also modelled as a function of M_{SLP}. The regression equations used were: $\mu_q = a + b \times M_{SLP}$ and $\sigma_q^2 = c \times M_{SLP}$, where *a*, *b* and *c* are regression parameters. The standard deviation (SD) can be obtained as the square root of the predicted variance.

Additive	Mean model (μ_q)	Variance model (σ_q^2)
DPA	$\mu_{q,DPA} = 0.536 + (1.497 \times 10^{-3}) \times M_{SLP}$	$\sigma^2_{q,DPA} = (7.344 \times 10^{-4}) \times M_{SLP}$
DBP	$\mu_{q,DBP} = 3.112 + (1.384 \times 10^{-2}) \times M_{SLP}$	$\sigma^2_{q,DBP} = (1.633 \times 10^{-1}) \times M_{SLP}$
EC	$\mu_{q,EC} = 0.207 + (8.373 \times 10^{-5}) \times M_{SLP}$	$\sigma^2_{q,EC} = (1.512 \times 10^{-4}) \times M_{SLP}$

which aligns with expectations. In contrast, T_{SLP} did not have a statistically significant effect on any of the additives ($p > 0.05$, partial $\eta^2 < 0.10$). The latter observation was somewhat unexpected, suggesting that formulation differences in SLPs either have a negligible effect on residue transfer at the individual compound level or are overshadowed by the stronger influences of M_{SLP} and H_{ID}.

3.4. Regression modelling

Since the previous analysis identified a strong relationship between q_T and M_{SLP}, a regression analysis was conducted to quantitatively model this trend and assess its potential for refining the estimation of expected q_T ranges when M_{SLP} is known. The aim was to derive predictive equations for both the expected mean and variance of q_T, enabling more precise data interpretation in forensic casework. To this end, various regression models – including linear–linear, linear-log, log-linear, and log–log – were tested on data pooled across T_{SLP} and H_{ID} (Fig. 4; see also Table 2). Pooling across T_{SLP} was justified by the previous analysis, which showed that this factor had no significant impact on q_T. Conversely, while H_{ID} was found to be significant, it remains an

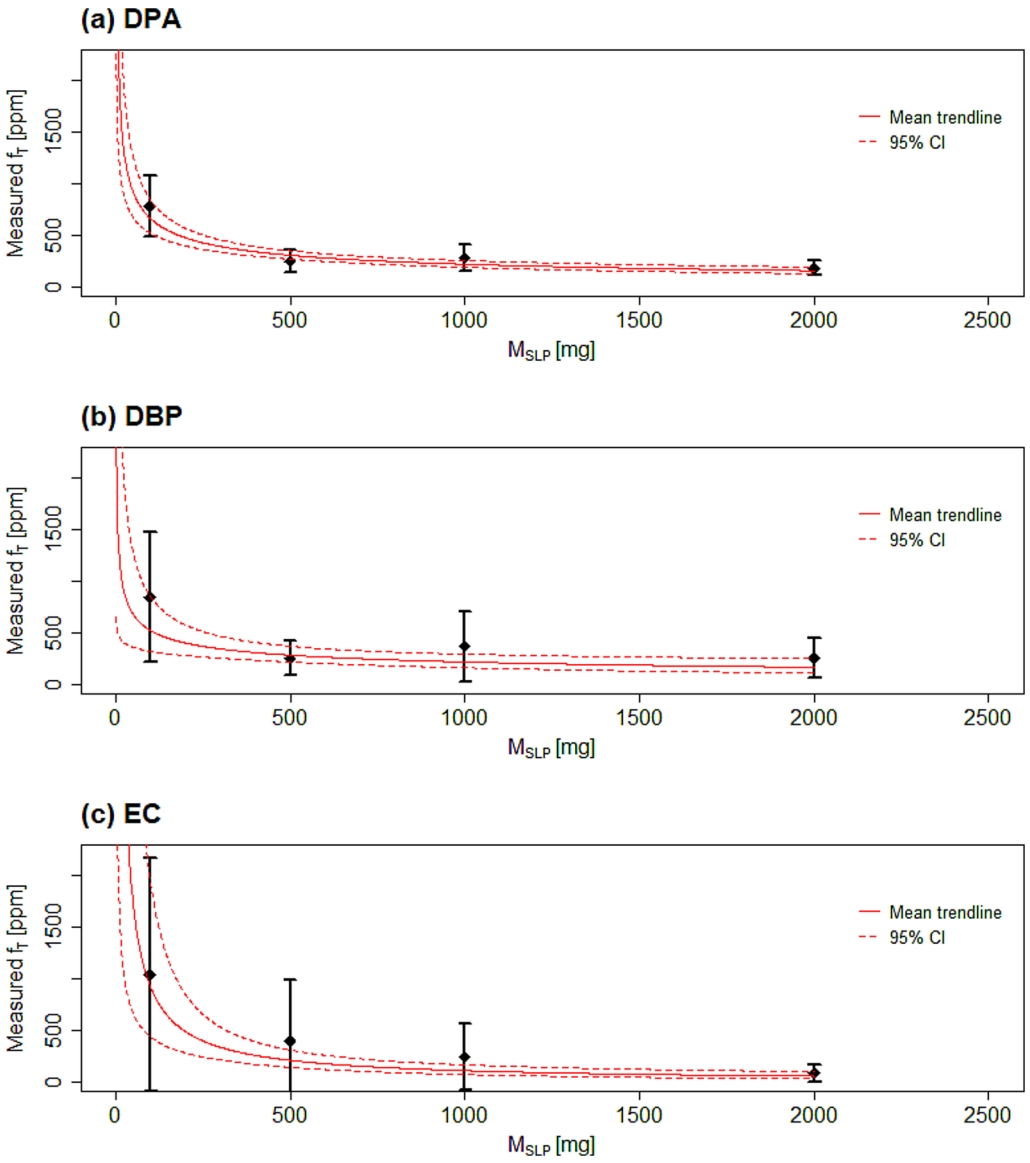


Fig. 5. Transfer efficiencies (f_T) for the three additives plotted against the total mass of SLP handled (M_{SLP}), based on data pooled across the different combinations of handler (H_{ID}) and SLP type (T_{SLP}). Error bars represent the standard deviations of the measured values. The solid red lines represent the mean trendlines, while the gray dotted lines correspond to the standard deviation (SD) trendlines. All these trendlines were derived from linear-linear regression models, which were identified as the best fit among those tested (see Table S5).

unavoidable source of variability in forensic casework, as accounting for it would require controlled tests with suspects handling explosives, which is generally not feasible in real world investigations.

Regression analysis showed that linear–linear models consistently yielded the highest model significance p-values (typically: $p < 0.05$) and the lowest lack of fit p-values (typically: $p > 0.1$) among those tested (Table S3). This confirmed that they provided the best fit across all three additives and accurately captured the dependence between q_T and M_{SLP}, further supporting the hypothesis that this relationship is predominantly linear (or near-linear) within the tested range. Ultimately, these findings demonstrate that regression analysis can be effectively used to exploit this, allowing for more precise estimations of expected q_T ranges when M_{SLP} is known. The models developed for each additive, summarised in Table 4, enable the estimation of both the expected mean and variance of q_T at any given M_{SLP} with strong predictive accuracy. This was further confirmed by a comparison of measured and predicted values across the M_{SLP} range, which showed a very close agreement (Table 2; see also Fig. 4). While the models perform well within the tested M_{SLP} range, future studies should extend it beyond 2000 mg to determine whether the linear trend persists or if a saturation point is eventually reached.

As an example of application, consider a situation where a POI is arrested, and hand swabs are collected to determine whether they have handled an SLP-based IED or not. Estimating the expected q_T range is a crucial first step in evaluating the significance of the analytical findings. If no information is available regarding M_{SLP}, the general statistics reported in Section 3.2 provide an initial reference for interpretation. For instance, in the case of DPA, the observed distribution of q_T is 1.883 ± 1.362 (SD) μg, offering a broad indication of what could be expected under generic handling conditions. However, if investigators have reason to believe that the POI came into contact with a specific amount of SLP, a more refined estimate can be obtained using the regression models presented earlier. Assuming an M_{SLP} of 1,500 mg, the model for DPA predicts an expected distribution of q_T of 2.782 ± 1.050 μg (SD), where the standard deviation is derived from the predicted variance.

This approach is consistent with methodologies reported in the literature, such as those by Biedermann & Taroni [42] or Gallidabino *et al.* [43], where similar quantitative estimates were subsequently integrated into Bayesian interpretation frameworks to assign evidential

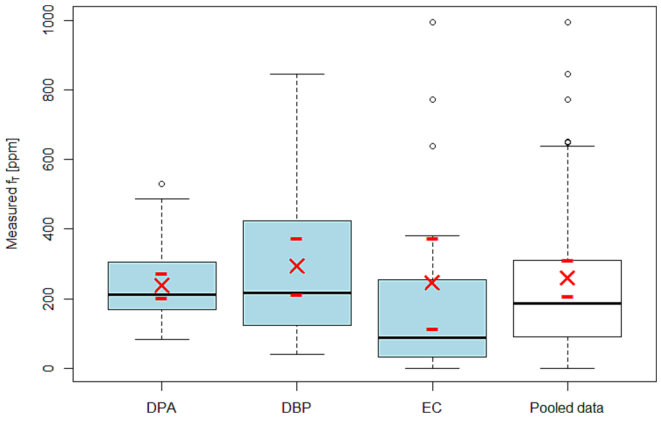


Fig. 6. Distributions of the transfer efficiencies (f_T) for each targeted additive ($n = 36$) and for all additives pooled together ($n = 108$), observed within the M_{SLP} range of 500–2000 mg. The red crosses indicate the mean values of each distribution, while the red lines represent the respective 95 % confidence intervals. The f_T values are expressed in parts per million (ppm), where 1 % corresponds to 10,000 ppm.

values through likelihood ratios.

3.5. Estimation of the transfer efficiencies

To gain deeper insight into the transfer mechanism, the transfer efficiencies (f_T) of the individual additives were calculated by dividing the q_T values by the corresponding amounts of additive effectively handled (Eq. (1)). In contrast to the q_T values, which increased proportionally with M_{SLP}, the f_T values exhibited a non-linear decline across the tested range, rapidly stabilising into an asymptotic plateau around $M_{SLP} = 500$ mg (Fig. 5; see also Table 2). Beyond this point, the f_T values for all three additives displayed reduced variability and remained largely constant, indicating that the fractions transferred to hands were no longer significantly influenced by external factors. Notably, the f_T profiles for the three additives were nearly identical, demonstrating greater inter-compound consistency across the M_{SLP} range compared to the corresponding q_T values. This suggests that the fraction of an additive transferred to hands is not only relatively stable across different conditions, but also minimally affected by its chemical nature or initial concentration in the SLP.

These findings support the potential utility of using generalised f_T estimates to predict the q_T ranges of other additives in SLP formulations and/or across different situations, an approach that merits further exploration in future studies. Based on the plateau region observed between $M_{SLP} = 500$ and 2000 mg, the measured f_T values were 238 ± 110 (SD) ppm for DPA, 294 ± 244 (SD) ppm for DBP and 245 ± 398 (SD) ppm for EC (Fig. 6). When pooling the data across all three additives, the global average f_T was 259 ± 275 (SD) ppm.

4. Conclusions

In this work, volunteers handled bulk SLP samples, and the quantities transferred to hands (q_T) of three common SLP additives (DPA, DBP, and EC) were systematically assessed using a simple swabbing method combined with a streamlined filter-and-shoot analytical approach. The results showed that q_T values typically ranged from high nanogram to low microgram levels, with DBP exhibiting the highest values and EC the lowest, mirroring their relative concentrations in the SLP formulations. The total mass of SLP handled (M_{SLP}) and the handler variability (H_{ID}) were found to generally have a highly significant effect on q_T, whereas the type of SLP (T_{SLP}) had a comparatively minor influence. Notably, a strong linear dependence between q_T and M_{SLP} was observed for all the three compounds and regression models were developed for the estimation of both the expected mean and variance of q_T at any given M_{SLP}.

This study provides essential empirical data on the primary transfer of SLP residues to hands, addressing a significant knowledge gap in forensic explosive analysis. The findings highlight the importance of considering contextual factors when interpreting analytical results and enable the estimation of expected q_T ranges on a POI's hands under the hypothesis that they had handled SLP across a range of scenarios. This, in turn, provides a robust foundation for interpreting questioned findings in real forensic casework. Specifically, the data generated in this work could be integrated into a probabilistic interpretation framework to support the assignments of likelihood ratios, thereby promoting a more transparent and objective evidential assessment [17,18]. To fully realise this approach, future research should focus on quantifying background levels of SLP additives on hands, assessing their retention and persistence following transfer, and gaining insight into actual SLP exposure levels during IED preparation. Moreover, extending these investigations to other explosive-related compounds would enhance interpretative capability across a broader range of forensic scenarios. In this context, the streamlined filter-and-shoot method developed in this study demonstrated strong potential for improving analytical throughput, positioning it as a valuable tool for future applications.

Ethics statement

This work was approved by the Health Faculties Research Ethics Subcommittee of King's College London (ref. no. HR/DP-22/23-36799).

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scijus.2025.101262.

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Quantification of smokeless powder (SLP) additives on hands after direct handling of bulk samples via a filter-and-shoot method

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