



# Improving first responder forensic capabilities: On-site detection and quantification of explosive precursors using portable near-infrared spectroscopy and machine learning

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## ABSTRACT

In this study, we assess the effectiveness of portable near-infrared (NIR) spectroscopy coupled with advanced machine learning algorithms for on-site detection and quantification of key explosive precursors, in accordance with EU Regulation 2019/1148. The research focuses on developing robust quantitative models for hydrogen peroxide, nitromethane, and nitric acid, addressing the challenge of varied concentrations and compositions encountered by first responders. The models demonstrated high predictive accuracy, with Root Mean Square Error of Prediction (RMSEP) values of 0.96 % for hydrogen peroxide, 2.46 % for nitromethane, and 0.70 % for nitric acid across diverse samples. The qualitative models created for those explosives precursors also showed high effectiveness and reliability, with minimal false negatives and false positives. The integration of machine learning algorithms facilitated the adaptation of these models to handle the complex variability of precursor formulations effectively. Additionally, the utilization of cloud operating systems provided significant advantages for real-time analysis and continuous data updating, essential for maintaining the accuracy and relevance of the models in rapidly changing field conditions. This research highlights the potential of integrating advanced spectroscopic techniques and machine learning within a cloud-based framework to improve the detection and management of explosive precursors in field settings. This integration enables the reliable detection and quantification of these precursors in a matter of seconds. Future work will extend this approach to additional precursors and explore complementary technologies to further enhance on-site detection capabilities.

## 1. Introduction

Homemade explosives (HMEs) are of interest to criminals and terrorists because of the accessibility of manufacturing recipes on the internet, the ease of obtaining the necessary equipment, and the availability of precursor materials for their synthesis. To disrupt the production of such HMEs, the European Union issued in 2019 a regulation on marketing and use of explosives precursors. This regulation entered into effect on February 1st, 2021. The substances covered by this regulation are now controlled by regulating access to high concentrations for 'Restricted Precursors', and by monitoring the sales of 'Reportable Explosives Precursors' (c.f. Table 1) [1]. The European Union considers that, beyond a threshold value, the risk of illicit manufacturing of explosives outweighs their legitimate use by the

public. As a result, under EU Regulation 2019/1148, the classification of a product as an explosive precursor is concentration dependent. This results in situations where the product's use may be deemed either legal or illegal.

Therefore, it is essential for first responders not only to be able to determine the identity or qualitative composition of a product quickly, safely and on the spot, but also to be able to establish whether the product is within the legal concentration limits. This determination is moreover critical in identifying potential safety hazards associated with elevated concentrations. In addition to the identification of an unknown product, the reliable quantification of that product enables first responders to take appropriate safety measures to mitigate any risks. However, on-site detection faces significant challenges, including the high cost and practical risks associated with traditional portable devices

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such as Raman (using a powerful laser source) on energetic materials [2, 3]. Other challenges include issues such as fluorescence interference with Raman, as well as strong water absorption in the infrared range. These factors can hinder detection and make quantification even more difficult [4–6].

A review of previous studies reveals that traditional portable Raman spectrometers are highly effective for the identification of unknown substances and have been successfully applied for the identification of listed precursors [7]. For the quantitative aspect, Stewart et al. [8] created a quantification model of hydrogen peroxide, using a portable Raman, and they were able to develop a good model with an average error of less than 1 % using an internal standard. However, operational implementation of the model directly on the portable Raman was not possible due to the device being primarily limited to file storage and library searching [8]. Therefore, there is a need for innovative and affordable approaches that enable rapid, reliable, sensitive and safe detection in the field [2,3,9].

In this context, near-infrared spectroscopy (NIR) emerges as a promising approach, delivering fast identification through portable devices and even allowing for the possibility of quantifying materials. Its effectiveness has already been highlighted for explosives precursors in the literature, for example, with hydrogen peroxide [10,11] or nitric acid [12]. This technology is portable, offers fast analysis (within a few seconds), is non-destructive, and is more affordable than Raman as it only uses halogen or tungsten lamps. Fluorescence issues are absent [13], and the intensity of water bands do not overwhelm the spectra as in mid-infrared spectroscopy, enabling various methods for measuring aqueous solutions [14,15]. Additionally, it produces high-quality spectra across different types of samples, making it highly valuable for quantitative analysis [16].

In addition, leveraging cloud technology enables to combine a NIR measurement devices with centralised computing capabilities. This opens up new possibilities for on-site detection and quantification of explosive precursors. Such architecture enables the use of advanced

machine learning models and algorithms to improve the detection and quantification of substances in the field [17,18]. It is characterized by faster response times, larger storage capacity for substances and mixtures, and built-in preprocessing of spectra [18]. However, it may also have potential limitations, such as security issues, a potential loss of control over the data and internet dependency [19,20].

The aim of this study is to assess the potential of portable NIR technology coupled with advanced multivariate data processing for on-site detection and quantification of explosives precursors. The study primarily focusses on hydrogen peroxide, a key precursor in the synthesis of various HMEs [7]. We have also explored the potential applicability of this approach for two other liquid precursors: nitromethane and nitric acid.

## 2. Materials and methods

### 2.1. Handheld near-infrared spectroscopy device

The portable instrument used in this study is the MicroNIR OnSite-W produced by Viavi Solutions Inc. (Scottsdale, Arizona, USA), featuring Bluetooth connectivity. It incorporated two vacuum tungsten lamps as a light source and a 128-pixel InGaAs photodiode array detector, which includes a Viavi linear variable filter (LVF). The detector operates in a wavelength range of 950 – 1650 nm (or 10.526 – 6060 cm<sup>-1</sup>) and has a spectral resolution of 6.2 nm for this span. The device has a signal-to-noise ratio of 25,000, an integration time of 10 ms, and performs 100 scans per analysis. It is powered by a Lithium-ion battery with a capacity of over 10 h and weighs 250 g [22,23].

For liquid analysis, a droplet accessory is added on the portable MicroNIR OnSite-W. It incorporates a built-in diffuse reflectance reference, and an integrated light pipe [24]. For this study, 100 µl of liquid was used for analysis.

To account for both sample variability and device variability, each sample was analysed three times using the same device and the process

**Table 1**

Restricted and reported explosives precursors with their concentration limitation in mass percentage (w/w) [1,21].

		Restricted precursors			Reportable explosives precursors	
		Public access	Access with authorisation	Illegal	Public access	
Acid	Nitric acid	≤ 3%	3% - 10%	> 10%	Reagent	Hexamine
	Sulfuric acid <sup>(1)</sup>	≤ 15%	15% - 40%	> 40%		Acetone
Oxidizer	Hydrogen peroxide	≤ 12%	12% - 35%	> 35%	Oxidizer	Potassium nitrate
	Ammonium nitrate	≤ 45.7 % <sup>(2)</sup>	No authorisation	> 45.7 %		Sodium nitrate
	Potassium chlorate	≤ 40%	No authorisation	> 40%		Calcium nitrate
	Sodium chlorate	≤ 40%	No authorisation	> 40%		Calcium ammonium nitrate
	Potassium perchlorate	≤ 40%	No authorisation	> 40%		Magnesium nitrate hexahydrate
	Sodium perchlorate	≤ 40%	No authorisation	> 40%		
Fuel	Nitromethane	≤ 16%	16% - 100%	-	Fuel	Magnesium powders <sup>(3)</sup>
						Aluminium powders <sup>(3)</sup>

(1) Sulfuric acid is not restricted in Switzerland (RS 941.421, 2022).

(2) 16% w/w nitrogen from ammonium nitrate corresponds to 45.7% ammonium nitrate, after removal of impurities.

(3) With a particle size of less than 200 µm, and for a substance or in mixtures containing 70% w/w or more of aluminium or magnesium.

was repeated across multiple devices.

## 2.2. Samples

All concentration levels are expressed as volume/volume percentage (% v/v) unless otherwise specified.

### 2.2.1. Hydrogen peroxide

Samples of different concentrations of laboratory grade hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solutions purchased from various suppliers were analyzed. These included 3 bottles of 60 % (Solvay chemicals, Inc.), 4 bottles of 50 % (Solvay chemicals, Inc.), 2 bottles of 35 % (Chem-Lab NV.), 1 bottle of 35 % (Sigma-Aldrich), 1 bottle of 35 % (Acros Organics), 1 bottle of 35 % (Vaprox), 4 bottles of 30 % (Sigma-Aldrich), 1 bottle of 30 % (Fluka) and 1 bottle of 12 % (Acros Organics). To obtain a wider range of concentrations for the construction of a quantification model, dilutions of these laboratory grade solutions were prepared with deionized water. The following dilutions were prepared (in v/v): 1 %, 5 %, 10 % (2x), 12 %, 15 %, 18 %, 20 %, 25 %, 28 %, 40 % and 55 %.

In addition, commercially available products containing hydrogen peroxide within the legal threshold of 12 % were purchased from the market. These included 11 hair oxidant creams/liquids, 1 stain remover, 1 oxygenated solution and 1 contact lens solution.

### 2.2.2. Nitromethane

Pure laboratory grade nitromethane solutions were purchased and analysed, which included 1 bottle of 99 % (Sigma-Aldrich) and 1 bottle of 99 % (Merck). These solutions were subsequently diluted in Methanol (Sigma-Aldrich) to obtain a wider range of concentrations. The following dilutions were prepared (in v/v): 0.5 %, 1 %, 3 %, 5 % (2x), 10 %, 15 %, 20 %, 25 %, 30 %, 35 % (2x), 40 %, 45 %, 50 %, 55 %, 60 %, 65 %, 70 %, 75 %, 80 %, 85 %, 90 % and 95 %.

In addition, 10 commercial samples of nitromethane, used as a fuel for scale models, were purchased locally. Seven of them had a concentration within the legal threshold of 16 %, one had a concentration of 20 % and the last two of 25 %. These commercial samples were all mixed with methanol, but GC-MS analysis revealed the presence of additional compounds in some samples, including lubricants oils, ricin oil, anti-wear agents, and antioxidants.

### 2.2.3. Nitric acid

A 65 % nitric acid laboratory grade solution (Fluka) was used to prepare a series of diluted solutions with deionised water. The following dilutions were prepared (in v/v): 3 %, 6.5 %, 10 %, 16.25 %, 26 %, 32.5 %, 39 %, 45.5 %, 48.75 %, 52 %, 58.5 % and 65 %.

## 2.3. Reference quantitation method

For hydrogen peroxide, accurate quantification was achieved in all hydrogen peroxide samples by titration with potassium permanganate ( $\text{KMnO}_4$ ). Titration was carried out in triplicate and by two persons as recommended by Solvay chemicals, Inc. [25].

Given the exploratory aims of our study, the quantitative analysis was strategically focused on commercial samples of nitromethane using gas chromatography-mass spectrometry (GC-MS), detailed in Annex A in the [supplemental material](#).

For laboratory-diluted mixtures of nitromethane and nitric acid, comprehensive quantitative evaluation was not prioritized. These substances were incorporated primarily to assess the viability of detection and quantification methods. However, these mixtures were prepared from laboratory-grade materials and handled under strictly controlled conditions to maintain consistency and reliability in our observations.

## 2.4. Multivariate data treatment

The software “Orange Data Mining” (version 3.36.2) was used to pre-process spectra. The pretreatment tested included smoothing, derivatives and various combination of those pretreatment as seen in [26].

This software was also used to create and test several machine learning models. These included Partial Least Square Regression (PLS-R), Support Vector Machines (SVM) with multiple kernel algorithms (such as Linear, Polynomial, Radial Basis Function, and Sigmoid), k-Nearest Neighbors (kNN), Decision Tree, Random Forest (RF), Gradient Boosting, Linear Regression, AdaBoost, Neural Networks (NN), Stochastic Gradient Descent, and even Stacking ensemble of some of these models.

Through the NIRLAB interface, advanced machine learning algorithms and libraries were also tested such as scikit-learn library (version 1.4.2) [27]. This library was chosen for its ability to handle complex predictive tasks, using advanced ensemble techniques such as stacking and bagging to enhance accuracy.

The Kennard-Stone selection method (66.6 % for calibration and 33.3 % for validation) was used to create a calibration set and an independent validation set. This allows for a maximal variability of the sample in each set [22,28]. This selection procedure was implemented using a Python (version 3.11.4) custom made script, which ensured that duplicate samples were not split during selection to prevent model overfitting. All calibration sets were validated with a leave-one-out cross-validation k-fold.

## 3. Results

### 3.1. Implementation of quantification models via qualitative assessment

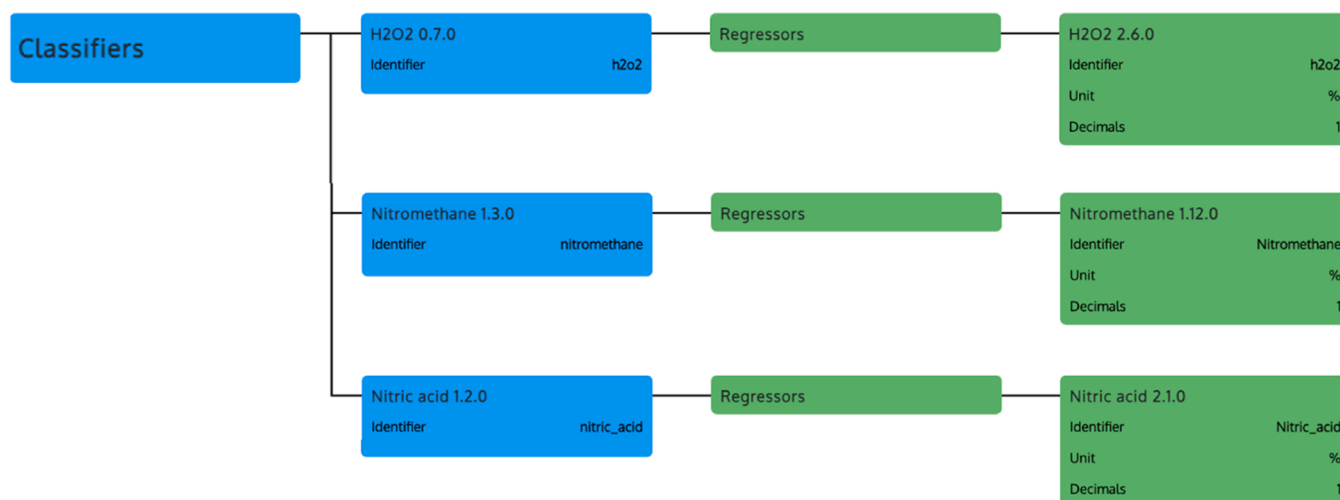
Before applying quantitative models, it is crucial to confirm that the substance under investigation has been accurately identified. This highlights the importance of considering qualitative aspects, as they influence the choice of quantification models. In our case, we opted for the implementation of a sequential approach illustrated in [Fig. 1](#), which involves a series of classification models for identification (in blue) followed by a regression model specific to the identified substance for quantification (in green).

To achieve this structure, we employed the same data sets used for quantification throughout the article to develop distinct analyte classification models ( $n = 44$  for hydrogen peroxide,  $n = 36$  for nitromethane and  $n = 12$  for nitric acid). For hydrogen peroxide, we incorporated 23 additional new samples, including laboratory-grade dilutions and commercial products, to enhance the sample size for model creation.

Additionally, we created sets of non- $\text{H}_2\text{O}_2$  samples, non- $\text{CH}_3\text{NO}_2$  samples and non- $\text{HNO}_3$  specimens to test the selectivity of the classification models. These sets included water, methanol, various acids (e.g.  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HCl}$ ), other explosive precursors, explosive powders, and non-explosive liquids/powders, with sample sizes of  $n = 1009$ ,  $n = 1040$  and  $n = 1068$ , respectively.

The Kennard-Stone selection method was used to create a calibration set and an independent validation set, essential for evaluating the performance of each model. The confusion matrices presented in [Tables 2, 3 and 4](#) provide a qualitative assessment on the calibration and independent validation sets of hydrogen peroxide, nitromethane and nitric acid.

[Tables 2 and 4](#) demonstrate high effectiveness, reliability and selectivity in predicting the presence of the analyte of interest, with minimal false negatives and no false positives. The models achieved an overall accuracy of 0.994 for hydrogen peroxide and 0.997 for nitric acid. The false negatives occurred with low-concentration solutions, which are not critical in this context, as these solutions are legal and



**Fig. 1.** Practical implementation based on a series of classification models (identifiers), which determine the appropriate regression model (regressors) used for quantification.

**Table 2**

Confusion matrix of hydrogen peroxide prediction (calibration and independent validation sets), with TP=True Positive, FN=False Negative, FP=False Positive, TN=True Negative, Precision=TP/(TP+FN), Negative predictive value=TN/(TN+FN), Sensitivity=TP/(TP+FN), Selectivity=TN/(TN+FP), Accuracy (TP+TN)/(TP+TN+FP+FN).

Actual	NIR Prediction (stacking of RF and NN)		
	H <sub>2</sub> O <sub>2</sub> (n=61)	Non-H <sub>2</sub> O <sub>2</sub> (n=1015)	
H <sub>2</sub> O <sub>2</sub> (n=67)	TP=61	FN=6*	Sensitivity=0.910
Non-H <sub>2</sub> O <sub>2</sub> (n=1009)	FP=0	TN=1009	Selectivity=1
	Precision=1	Negative predictive value=0.994	Accuracy=0.994

\* 1%, 3%, and three 5% laboratory-grade dilutions and one 3% commercial sample

**Table 3**

Confusion matrix of nitromethane prediction (calibration and independent validation sets).

Actual	NIR Prediction (stacking of RF and SVM)		
	CH <sub>3</sub> NO <sub>2</sub> (n=38)	Non-CH <sub>3</sub> NO <sub>2</sub> (n=1040)	
CH <sub>3</sub> NO <sub>2</sub> (n=36)	TP=36	FN=0	Sensitivity=1
Non-CH <sub>3</sub> NO <sub>2</sub> (n=1040)	FP=2*	TN=1040	Selectivity=0.998
	Precision=0.947	Negative predictive value=1	Accuracy=0.998

\* Two methanol samples

**Table 4**

Confusion matrix of nitric acid prediction (calibration and independent validation sets).

Actual	NIR Prediction (stacking of RF and NN)		
	HNO <sub>3</sub> (n=9)	Non-HNO <sub>3</sub> (n=1068)	
HNO <sub>3</sub> (n=12)	TP=9	FN=3*	Sensitivity=0.750
Non-HNO <sub>3</sub> (n=1065)	FP=0	TN=1065	Selectivity=1
	Precision=1	Negative predictive value=0.997	Accuracy=0.997

\* 3%, 6.5%, 10% laboratory-grade dilutions

non-dangerous for first responders.

For nitric acid specifically, it will be necessary to include additional data to enhance model sensitivity, which is currently of 0.75, due to the limited number of samples (only 12) used to create this class.

The model for nitromethane (Table 3) achieved an accuracy of 0.998. It is highly effective with no false negatives and two false positives involving methanol solvents, which is the common solvent for nitromethane solutions. This false positive rate could potentially be reduced with additional data.

### 3.2. Quantification of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

Samples of hydrogen peroxide were analysed for concentrations ranging from 1 % to 60 %. Higher concentrations were not available from chemical suppliers. Fig. 2 shows the average NIR spectra after Standard Normal Variate (SNV) normalization measured for 30 laboratory-grade samples of hydrogen peroxide of different concentrations. Although these spectra may appear similar at first glance, they exhibit notable differences, especially in the NIR range around 1450 nm, which is commonly attributed to the first overtone of O-H stretching [12]. As noted by Pimenta et al. [10] and Woo et al. [11], the presence of a high concentration of H<sub>2</sub>O<sub>2</sub> leads to a decrease in NIR spectra intensity in the 1400–1500 nm region, with a corresponding increase in the 1550–1700 nm region. However, it is difficult to attribute these changes to either water or peroxide, as both molecules interact in this NIR region [10]. Nevertheless, the results suggest the possibility of testing a quantification model, as there appears to be a linear relationship between the concentration of hydrogen peroxide and the corresponding intensity/shapes of the peaks (Fig. 2).

Several quantification models were created and tested on those 30 samples. This set yields a total of 39 measurement points to account for the device variability on a same sample. Each sample was subjected to prior titration to establish reliable reference concentration values.

Various preprocessing techniques, including smoothing, derivatives, and their combinations, were evaluated. As demonstrated in [26], the optimal model incorporated a combination of the second derivative Savitzky-Golay filter (second order, 7 points window) followed by normalization using Standard Normal Variate (SNV). The most effective model for this dataset was a Partial Least Squares (PLS) regression model with four factors (Fig. 3).

The performance of the model was assessed using a validation set

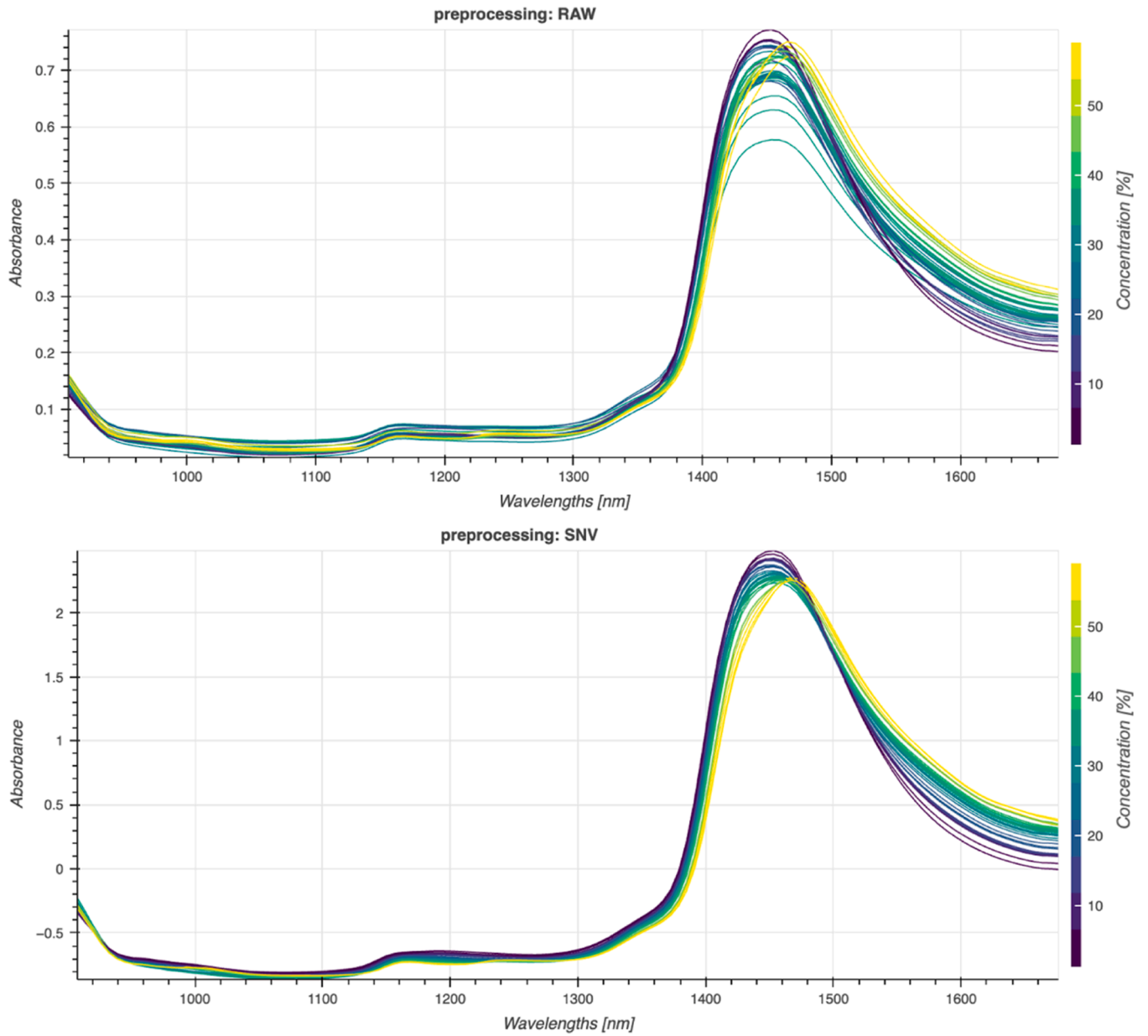


Fig. 2. NIR spectra of 30 samples of H<sub>2</sub>O<sub>2</sub> from 1 % to 60 % with no preprocessing (above), and Standard Normal Variate (SNV) preprocessing (below).

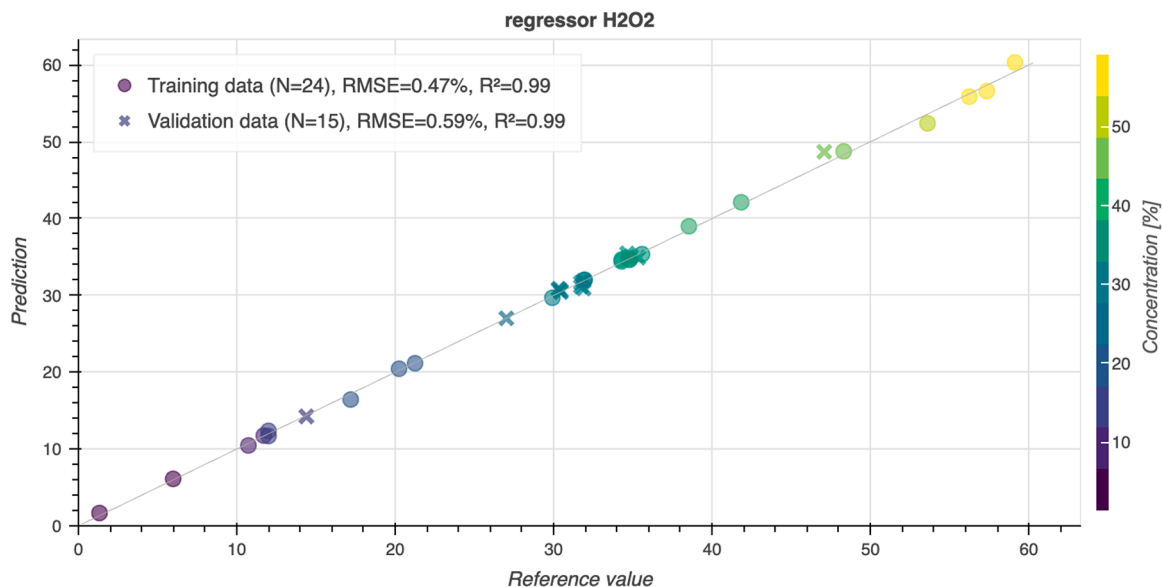


Fig. 3. PLS quantification model of H<sub>2</sub>O<sub>2</sub> (1-60 %).

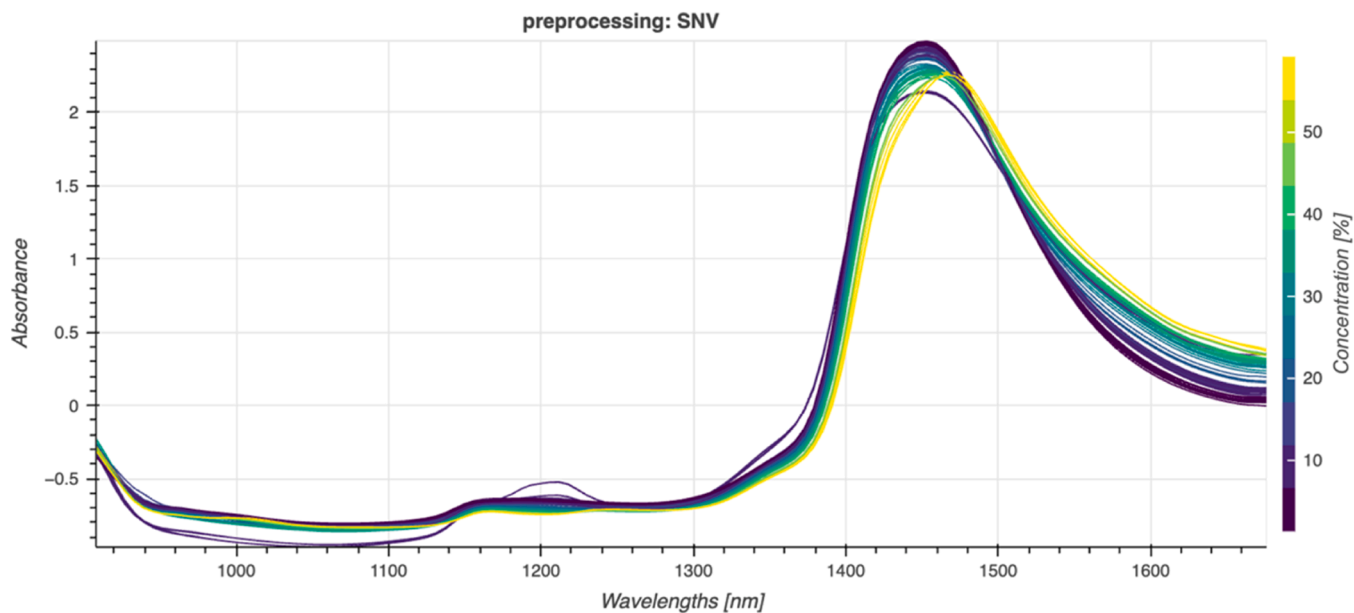


Fig. 4. NIR spectra of 30 samples of H<sub>2</sub>O<sub>2</sub> (1-60 %) and 14 commercial products (3.3-12.3 %), with SNV preprocessing.

created independently with the Kennard-Stone selection method. The error of prediction of this model for this validation set, measured by the Root Mean Square Error Prediction (RMSEP), was calculated at 0.59 %, along with a high determination coefficient ( $r^2$ ) at 0.99. The limit of detection (LOD) and quantification (LOQ) were calculated to be 1.76 % and 5.33 % respectively, following the guidelines of the European Medicines Agency (EMA) [29].

These statistical descriptors, combined with the number of factors used in the PLS model, yield promising results for the rapid prediction of new samples.

The ultimate evaluation of a model's effectiveness lies in its ability to analyze real-life samples that first-responders may encounter on-site. In this perspective, the goal was to construct a quantification model that

incorporates the variability and complexity of real-life samples, which was not previously considered as only lab-grade dilutions of hydrogen peroxide in water were used. Thus, commercially available products containing hydrogen peroxide were added to the model, as such products could also be encountered in real-life situations. However, other types of real-case samples, such as boiling-down solutions, were not studied in this research.

The purchased products included hair oxidant creams/liquids, a stain remover, an oxygenated solution and a contact lens solution. Titration was performed on these items to measure their hydrogen peroxide concentration, which ranged from 3.3 % to 12.3 %.

The composition diversity found in commercial specimens introduces variability, especially in the concentration range below 12 %,

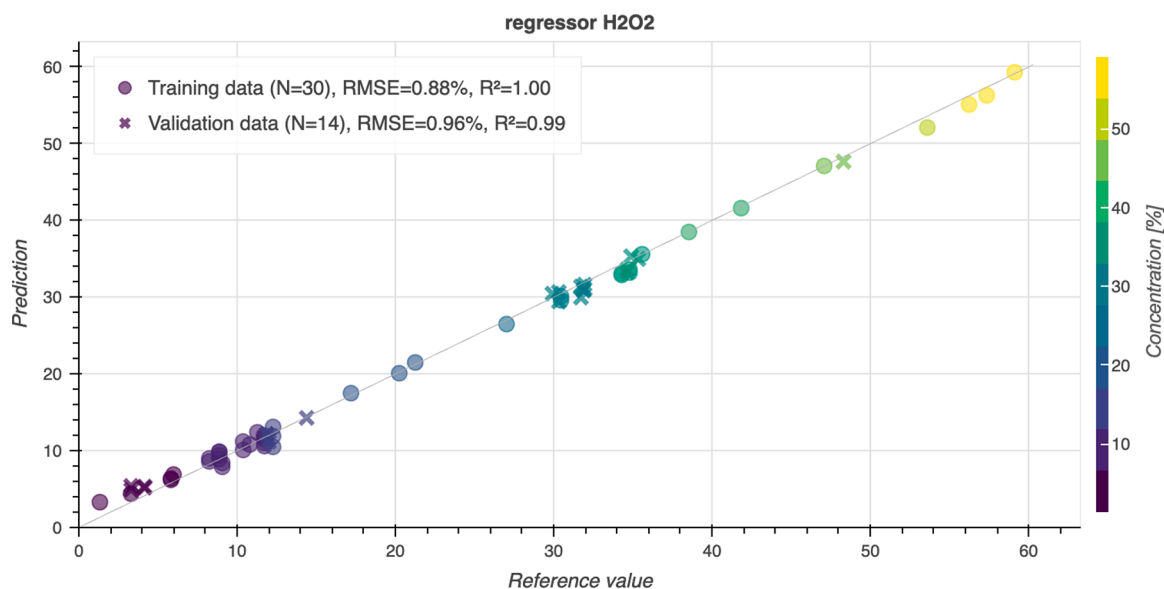


Fig. 5. Combination of advanced regression models of H<sub>2</sub>O<sub>2</sub> (1–60 %) and commercial products (3.3–12.3 %).

the maximum legal threshold indicated in Table 1. The dataset's underlying structure shows that establishing a direct linear relationship between the intensity/shapes of the peaks and the reference value is challenging due to the diversity in composition of the specimens (Fig. 4). The NIR spectra of the 14 commercial samples separately are available in Annex B in supplemental material.

The use of advanced regression models was required. Although various models, including Support Vector Machines (SVM) were tested, the best results were achieved by stacking multiple machine learning models. This was done by creating a custom pipeline that integrated three regressor models: random forest, gradient boosting and neural network. Using ensemble machine learning stacking through the scikit-learn library we developed a 'super model' with these three models, which demonstrated the best performance on the validation dataset.

For the creation of the validation set, the Kennard-stone method selected three out of the fourteen commercial products, the eleven others having been used for the model construction.

The final regression model, presented in Fig. 5, demonstrated excellent accuracy and performance, with a RMSEP value of 0.96 % and a  $r^2$  of 0.99. The calculated LOD and LOQ were calculated to be 2.57 % and 7.78 % respectively, following EMA guidelines [29].

This final model achieved comparable prediction performance to the previous Partial Least Square (PLS) model, showcasing its robust performance despite the added complexity introduced by the real-life samples. This is of significant importance for the practical application of the method in on-site analyses conducted by first-responders.

### 3.3. Quantification of nitromethane (CH<sub>3</sub>NO<sub>2</sub>)

Fig. 6 illustrates the average NIR spectra of 36 samples of nitromethane in methanol, with concentration ranging from 0.5 % to 99 %. Higher concentrations were not available from chemical suppliers.

This set of 36 samples included 10 commercial products, that underwent quantification using gas chromatography-mass spectrometry (GC-MS) to determine their nitromethane concentration. Results showed that seven products complied with the legal limit, featuring concentrations from 2.05 % to 14.02 %. One product, advertised as containing 20 % nitromethane, measured at 17.39 %, while two products labelled

at 25 % had concentrations between 19.61 % and 19.78 %. The NIR spectra of the 10 commercial samples separately are available in Annex C in supplemental material.

As outlined by Li et al. [30], the NIR absorption peaks of both methanol and nitromethane include the second overtone of the C-H bond in 1100–1220 nm. In the 1400–1600 nm range, methanol combines this with the first overtone of O-H bond [30], while nitromethane is associated with the first overtone of C-H bond. The intensity and shape of the spectra seem to correlate with the concentration of nitromethane (see Fig. 6). Around 1415 nm, we observe that the peak intensity increases with nitromethane concentration up to 80 %. However, there is a sudden decrease in peak intensity between 80 % and 99 % concentration. This specific behaviour suggests a particular interaction between nitromethane and methanol, which impacts the absorption in this wavelength region.

Several quantification models were created and tested on those 36 samples. This set yields a total of 51 measurement points to account for the device variability on a same sample. For the creation of a quantification model, the Kennard-stone method was used, as previously, to create a calibration set and an independent validation set. The validation set is composed of 5 commercial samples and 6 laboratory grade dilutions.

Numerous regression models were tested as mentioned in Methodology. The best performance was obtained with a SVM (polynomial kernel) (Fig. 7).

The quantification model achieved excellent performance, with a RMSEP of 2.46 % and a  $r^2$  of 0.99. The calculated LOD and LOQ [29] were respectively of 5.76 % and 17.45 %, aligning with the legal threshold of nitromethane (16 %, see Table 1).

This model demonstrated impressive predictive accuracy despite minor imprecisions potentially occurring during the preparation of the diluted solutions. These dilutions were prepared under strictly controlled conditions, but they were not verified against a reference method for error correction. This was due to the exploratory nature of this study, which prioritized the quantification of commercial samples.

Even so, the model achieved acceptable RMSEP, LOD and LOQ values, close to the legal threshold limit. This performance suggests good accuracy and efficacy in practical field applications.

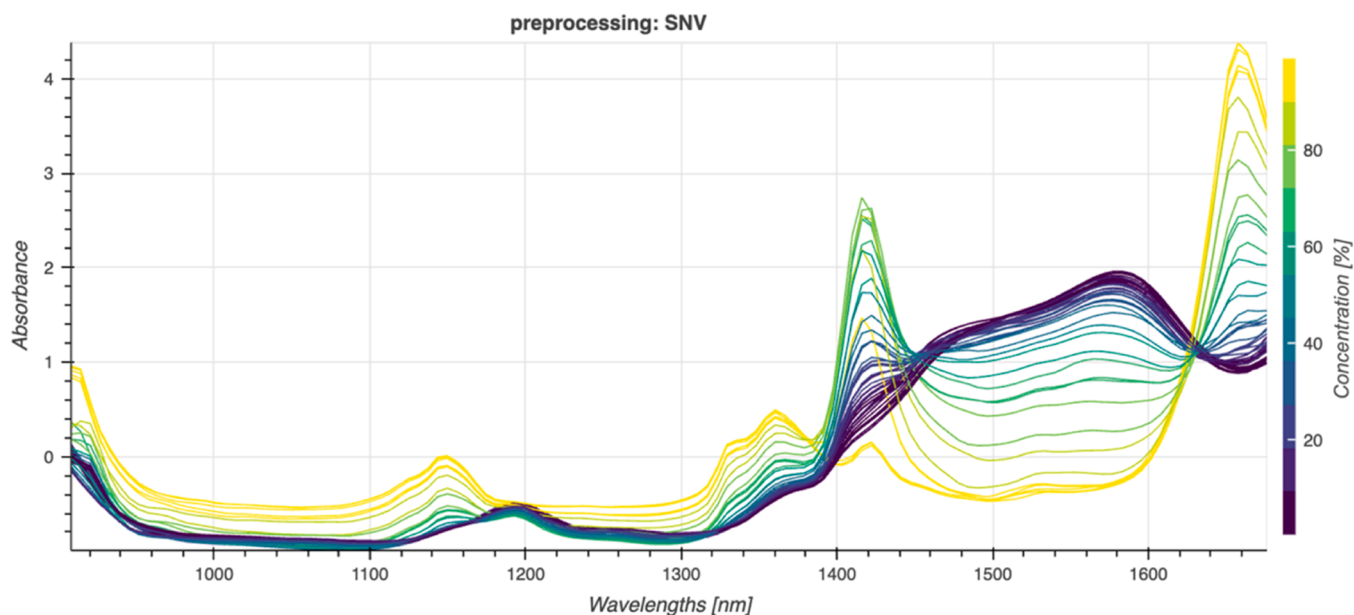


Fig. 6. NIR spectra of 26 samples of  $\text{CH}_3\text{NO}_2$  (0.5–99 %) and 10 commercial products (2.05–19.78 %), with SNV preprocessing.

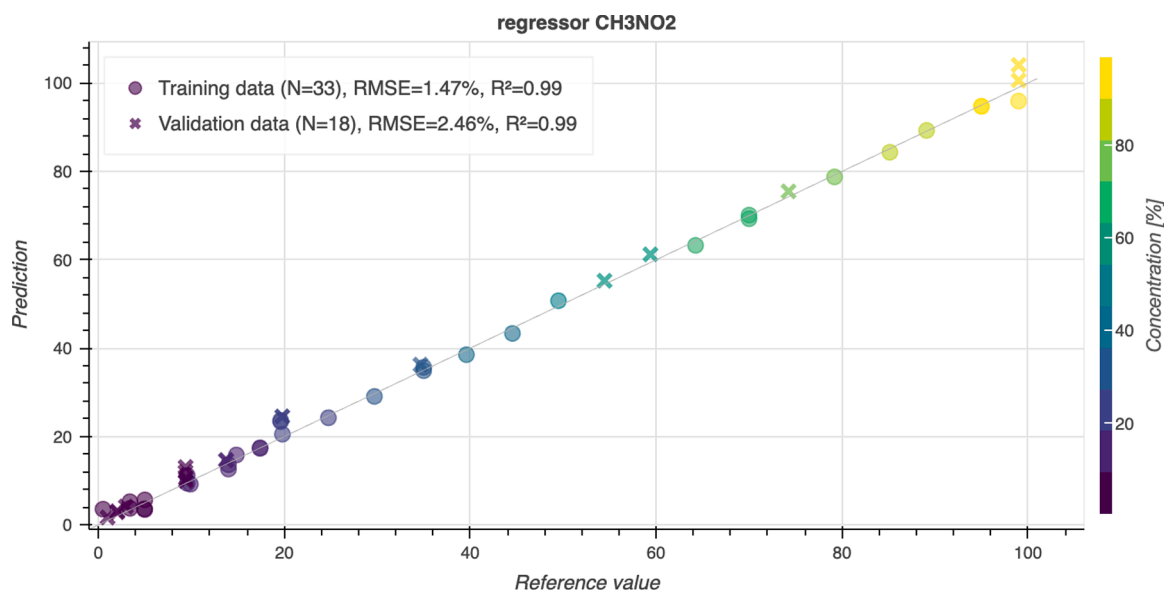


Fig. 7. SVM (polynomial kernel) regression model of  $\text{CH}_3\text{NO}_2$  (0.5–99 %) and commercial products (2.05 %–19.78 %).

### 3.4. Quantification of nitric acid ( $\text{HNO}_3$ )

The results of the average NIR measurement of 12 solutions containing nitric acid in water are depicted on Fig. 8. As only dilutions samples were considered, no reference method was employed. The measurements were limited to nitric acid concentrations of up to 65 % due to resource limitations in the lab. While this range was sufficient for developing a preliminary model, future studies will explore higher concentrations and assess any potential effects on the measuring instrument or the droplet accessory.

Similarly to hydrogen peroxide, significant spectral changes occurred around 1440 nm, which is associated with O-H stretching [12]. As previous research has shown [12,31], inorganic acids have an indirect influence on this spectral range. Although they do not absorb NIR radiation, inorganic acids interact with water molecules within this range, which affects the spectra. These interactions seem to be specific to

each inorganic acid [12]. For instance, Sadergaski et al. [12] compared the NIR spectra of sodium nitrate ( $\text{NaNO}_3$ ) and nitric acid ( $\text{HNO}_3$ ), both containing a nitrate ion, and found their NIR water band to be different.

A quantification model was created based on the significant changes in the NIR spectra related to variations in concentration (see Fig. 8). Several quantification models were examined and a simple PLS regression with 5 Factors was selected as an accurate model for the prediction of new samples (Fig. 9). The RMSEP value was calculated to be 0.70 % with a  $r^2$  of 0.99. Furthermore, the LOD and LOQ were calculated to be 2.35 % and 7.12 % respectively, following EMA guidelines [29].

Although the LOD and LOQ values align with the legal thresholds for nitric acid (3 % and 10 %, see Table 1), it is important to note that the model can still effectively distinguish between legal and illegal concentrations. Therefore, it provides valuable information for first responders.



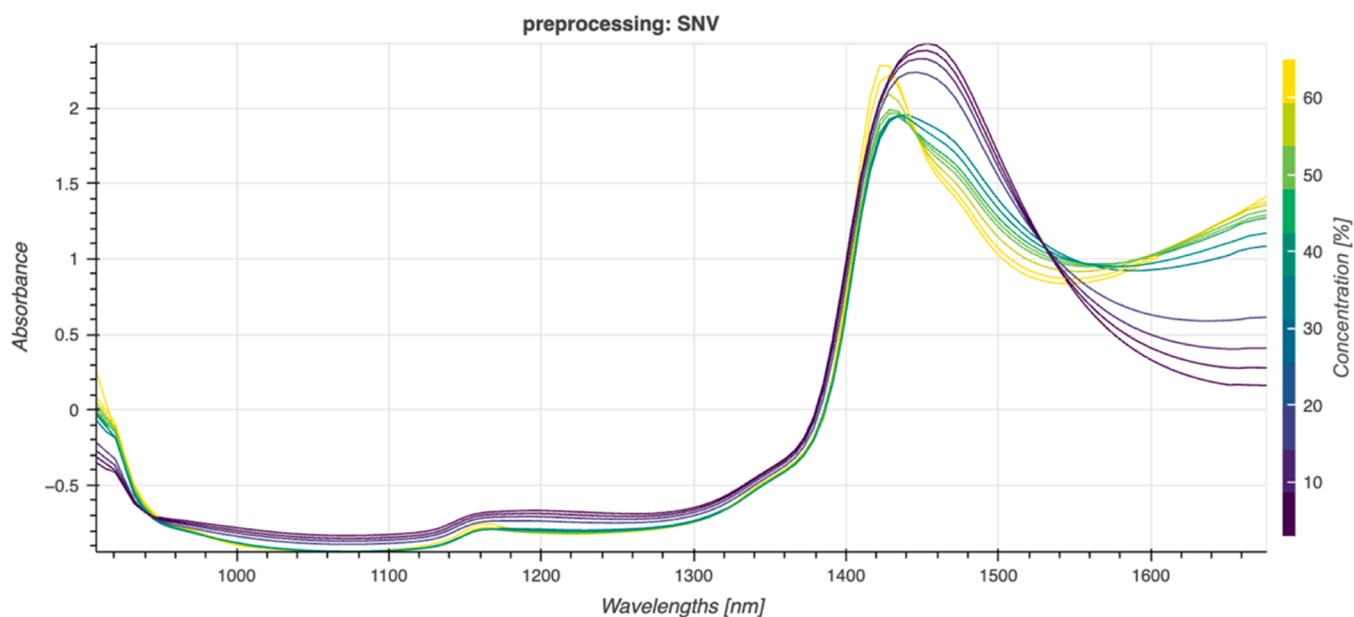


Fig. 8. NIR spectra of 12 samples of HNO<sub>3</sub> (3–65 %), with SNV preprocessing.

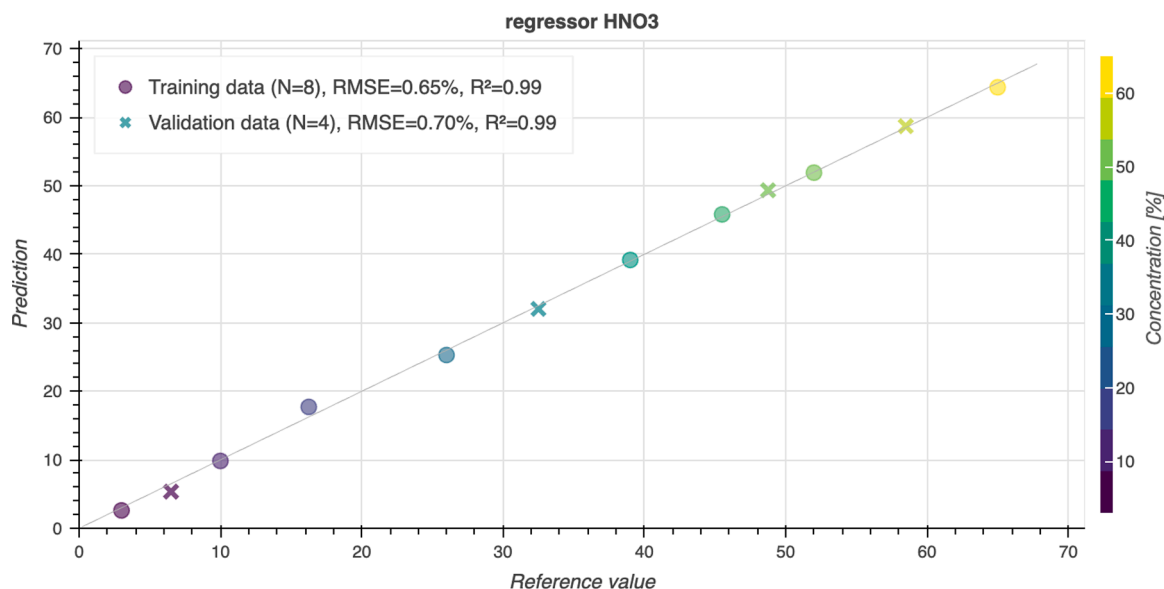


Fig. 9. PLS quantification model of HNO<sub>3</sub> (3–65 %).

#### 4. Discussion and conclusion

In response to "EU Regulation 2019/1148 of the European Parliament and of the Council on the marketing and use of explosives precursors," quantitative models have been developed for three critical precursors: hydrogen peroxide, nitromethane, and nitric acid. These models are specifically developed to accommodate a wide range of concentrations and product compositions that first responders might encounter on site. This includes samples around the regulated threshold values (refer to Table 1) and various commercially available products.

The development and implementation of these models faced numerous challenges due to the diversity in compositions and concentrations. However, the use of machine learning algorithms for data treatment has enabled the integration of this variability into robust quantification models. These models have demonstrated high accuracy in predictive performance, as evidenced by their Root Mean Square Error of Prediction (RMSEP) values: 0.96 % for hydrogen peroxide over

44 samples, 2.46 % for nitromethane over 36 samples, and 0.70 % for nitric acid over 12 samples. Additionally, the associated qualitative models demonstrated high effectiveness and reliability, with minimal false negatives and false positives. These results underscore the models' capability to handle diverse precursor formulations, highlighting their potential accuracy and reliability for field operations.

Regarding the practical implementation of these models, an offline operating system proved inadequate, as observed by Stewart et al. [8], due to rapid obsolescence and algorithm constraints [18,32]. In contrast, cloud operating systems offer significant advantages for implementation, including advanced model testing and real-time analysis through decentralized architecture [22,27]. They also facilitate the real time collection and sharing of measurements and metadata (including the nature and description of the sample, localization, time), paving the way for these measurements in a forensic intelligence perspective [33]. Cloud-based systems enable easy integration of new measurements and continuous updates, enhancing predictive

capabilities [22,32].

This aspect is of particular significance in the context of explosive precursors. Given the potential diversity in concentration and composition, a system that can adapt to emerging trends in the market or real-life scenarios becomes essential.

It is noteworthy that these explosive precursors can be synthesized through artisanal means using pre-precursors, such as perborates/peroxyhydrate carbonates diluted in water, or treated with acid, to produce H<sub>2</sub>O<sub>2</sub> [34]. These pre-precursors are not regulated and are freely available to the public, without any restrictions on their concentration or quantity. Consequently, it is crucial to have a detection and quantification ecosystem that can adapt to these evolving conditions as the availability of these substances may change over time, thus introducing possible new trends.

This study focused on NIR measurements. But, as noted by Hotchkiss [35], each detection technique has its own capabilities and limitations, and no single technique can meet all detection needs. This is also true for NIR technology which has demonstrated great capabilities for quantifying some explosive precursors, but currently requires a manipulation step when dealing with liquids. This may be a drawback for first responders as this approach involves a handling step that can lead to potential exposure to hazardous substances.

Further research is needed with other sensing technologies, such as Raman measurements, to determine if they could complement NIR and expand the range of quantifiable substances.

#### CRediT authorship contribution statement

**Olivier Delémont:** Writing – review & editing, Visualization, Validation, Supervision, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Bart Simoens:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **Pierre Esseiva:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Investigation, Conceptualization. **Florentin Coppey:** Writing – review & editing, Visualization, Supervision, Software, Investigation, Formal analysis, Conceptualization. **Jade Chevalley:** Writing – review & editing, Validation, Methodology, Investigation. **Alexandre Rochat:** Writing – review & editing, Visualization, Validation, Software, Methodology, Investigation. **Anne-Flore Prior:** Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Conceptualization.

#### Declaration of Generative AI and AI-assisted technologies in the writing process

Parts of the manuscript were proofread using ChatGPT 3.5 and 4.0. The authors subsequently reviewed and revised the content as needed, and they assume full responsibility for the accuracy and integrity of the final publication

#### Declaration of Competing Interest

The authors report no declarations of interest.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.forsciint.2025.112378](https://doi.org/10.1016/j.forsciint.2025.112378).

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