Determining temporal composition changes of a ternary mixture

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Abstract

A novel mosquito repellent formulation was developed that is applied via a liquid wick-based vaporizer. The formulation is a ternary mixture containing Lapa essential oil, an aliphatic carrier and an alcohol. It is essential that the formulation releases the active at a constant rate over a long period of time. To check this, the change in composition was followed over time. The composition, at various stages, was determined from FTIR spectra. An inverse mapping approach that employed partial least square regression (PLSR) was used. The results show that the active ingredient content of the oil mixture remained essentially constant over the oil application life time.

Keywords: Inverse identification; Partial least square regression; Composition; FTIR.

Introduction

In many industrial applications it is critical to study the variation of mixture composition over time. For instance, in order to investigate the efficiency and protection time of an insect repellent, it is of utmost important to track the active ingredient content of a repellent mixture over its application lifetime. Noteworthy is the fact that the optimum efficiency is achieved with a constant release rate of the active ingredient at the desired level.

Liquid wick-based vaporizers are appliances used to continuously release mosquito repellents. The vaporizers have a solid wick that extends to the bottom of the flask filled with the repellent oil mixture. Heating the top portion accelerates evaporation of the absorbed oil. Provided that the volatiles contain sufficient active ingredients, the released fumes will efficiently repel mosquitoes. However, the wick might selectively absorb certain mixture ingredients. In addition, the ingredients might evaporate at different rates. Therefore the wick and the oil mixture components should be selected such that active ingredients evaporate at the desired rate in fixed proportions defined by the initial mixture composition.

In this study an inverse mapping technique [Asaadi et al. (2014)] was employed to perform the inverse analysis required to determine the composition of the remaining liquid at three stages of liquid oil consumption.

Composition identification method

The oil mixture contained Lapa essential oil as active ingredient, an aliphatic carrier and an alcohol as stabilizer. Fourier transform infrared (FTIR) spectroscopy was used to characterize the composition of the mixtures. FTIR spectroscopy is an effective method for quantitative analysis of especially organic molecules as it is sensitive for functional groups. The FTIR spectrum of every compound is unique. Therefore it can be used as a fingerprint for a given chemical. However, quantitative interpretation of the FTIR spectrum of a mixture is not straightforward. In this study the FTIR spectrum of the repellent formulation represented the response determined by the composition of the oil mixture. The liquid phase FTIR spectra were recorded on a Perkin-Elmer Spectrum RX

100 spectrometer at room temperature in the wavenumber range 4000 to 650 cm^{-1} at a resolution of 2 cm^{-1}.

When direct measurement is not possible, inverse identification methods are used to identify system parameters from the response of the system. One approach for solving inverse problems is to use inverse mapping.

In this study the inverse mapping linked the FTIR spectra to mixture compositions via a mathematical model. The latter was constructed using partial least square regression (PLSR). PLSR is an intuitive method that is used to find major relations between parameters and the responses of the system. It develops a linear regression model projecting the parameters and the responses to a new space [Andrade-Garda JM (2009)]. PLSR was selected to solve the present inverse problem, since it is especially effective at dealing with large sets of information (e.g. complex FTIR spectra) that are used to predict a smaller set of parameters, e.g. the composition of the mixtures.

Constraining the inverse identification problem to identify the mass percentage of the ingredients

The construction of the inverse map using PLSR requires a suitable training set of FTIR spectra for mixtures of known composition. These were chosen using a factorial design for the ternary mixtures. A total of nine spectra for mixtures containing Lapa, carrier and alcohol were recorded. The spectra provided the inputs and the compositions, expressed in terms of mass percent, were the outputs of the inverse mapping. Accuracy was checked using cross validation to determine the optimum PLSR.

Results and Discussion

Samples were collected at three different stages of oil consumption namely after only ¾, ½, and ¼ of the initial volume remained. The compositions were determined by inverse mapping from their FTIR spectra. Table 1 shows the primary composition of the ternary mixture of the formulation as well as predicted compositions of the unknown samples. In order to validate the accuracy of the inverse identification, additional samples corresponding to the predicted compositions were prepared. Their FTIR spectra were recorded and compared to those of the unknown mixtures.

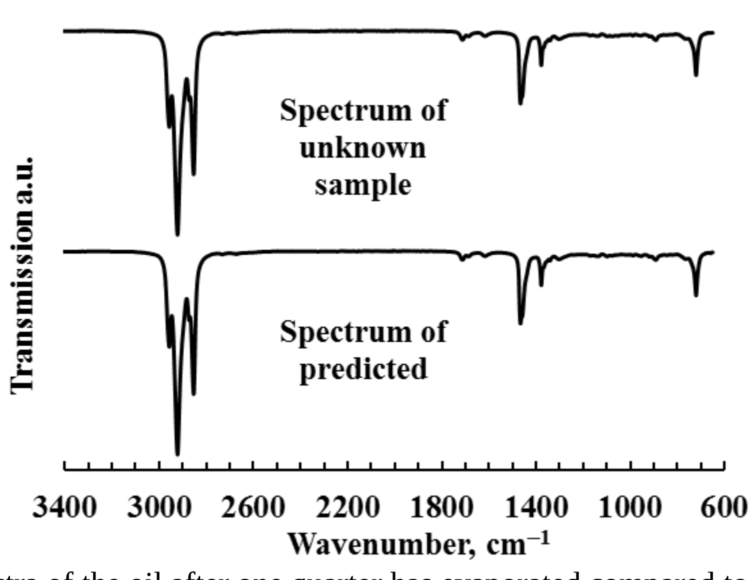

Figure 1. FTIR spectra of the oil after one quarter has evaporated compared to the sample made up on the basis of the predicted composition.

Figure 1 shows the good agreement of the spectra and this demonstrates that the inverse was accurate. This demonstrated that the active ingredient is continuously released at approximately a fixed rate. Considering the release rate of the repellent formulation shown in Figure 2, it is clear that the system can provide protection for more than two weeks.

Table 1. Primary composition and predicted compositions

Fraction original volume	Lapa	Alcohol	Carrier
1	2.23	4.28	93.5
0.75	1.98	4.63	93.4
0.50	2.04	4.52	93.4
0.25	2.41	4.27	93.3

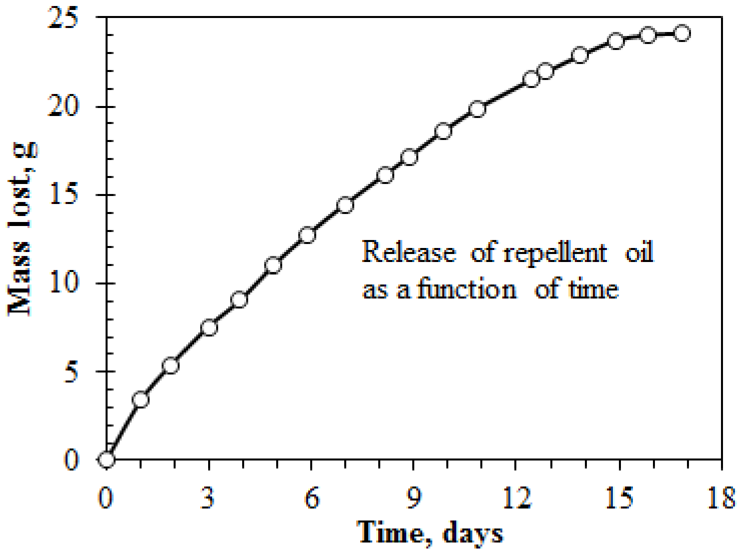

Figure 2. Repellent release curve in the liquid wick-based vaporizer initially filled with 25 g oil.

Conclusions

In this study PLSR was applied for tracing efficiency of a liquid wick-based vaporizer during its lifetime by considering mass percentage of the active ingredient of the oil mixture. Validation of the predicted compositions demonstrated that the adapted inverse method could accurately predict the oil mixture composition. Tracing the active ingredient of the mixture demonstrated that efficiency of the liquid wick-based vaporizer is kept almost constant during its lifetime.

Acknowledgments

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