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Synthesis route attribution of sulfur mustard by multivariate data analysis of chemical signatures☆

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ABSTRACT
A multivariate model was developed to attribute samples to a synthetic method used in the production of sulfur mustard (HD). Eleven synthetic methods were used to produce 66 samples for model construction. Three chemists working in both participating laboratories took part in the production, with the aim to introduce variability while reducing the influence of laboratory or chemist specific impurities in multivariate analysis. A gas chromatographic/mass spectrometric data set of peak areas for 103 compounds was subjected to orthogonal partial least squares - discriminant analysis to extract chemical attribution signature profiles and to construct multivariate models for classification of samples. For one- and two-step routes, model quality allowed the classification of an external test set (16/16 samples) according to synthesis conditions in the reaction yielding sulfur mustard. Classification of samples according to first-step methodology was considerably more difficult, given the high purity and uniform quality of the intermediate thiodiglycol produced in the study. Model performance in classification of aged samples was also investigated.
Abbreviations:
HD, Sulfur mustard; CWA, Chemical warfare agent; CWC, Chemical weapons convention; CAS, Chemical attribution signature; TDG, Thiodiglycol; OPLS-DA, Orthogonal partial least squares – discriminant analysis; PCA, Principal component analysis; PC, Principal component

Keywords:
Chemical forensics; Multivariate data analysis; Sulfur mustard; Synthesis method attribution

1 Introduction

Sulfur mustard (2,2'-dichloroethyl sulfide or bis(2-chloroethylsulfide), HD) is a vesicant commonly employed as a chemical warfare agent (CWA). Large amounts of HD were produced and stockpiled in several countries before the ratification of the Chemical Weapons Convention (CWC) in 1997 [1]. The convention bans the production, storage and use of CWAs, and the destruction of declared stockpiles is still an ongoing endeavor. HD is a relevant threat agent because its synthesis is a relatively simple process, and there are several synthetic routes that can be used for its production in large scale [4-6]. While access to the required precursors and reagents is limited by export control and the obligations of the State Parties of the CWC, many of these materials have widespread industrial applications, making barriers of trade less effective in controlling their use.

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