The use of GC-C-IRMS analyses for linking seizures of Ecstasy tablets

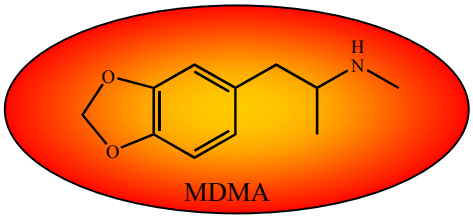
Fabien Palhol[1,2*], Martine Chabrillat[2], Norbert Naulet[1]

1 LAIEM, UMR 6006, Faculté des Sciences et des Techniques, 2 rue de la Houssinière, 44322 Nantes cedex 3, France

2 Laboratoire des Douanes de Paris, 1 rue G. vicaire, 75003 Paris, France *fpalhol@wanadoo.fr

Introduction

Ecstasy is today a major drug of abuse in Europe, and in France the number of tablets analysed by French Customs has increased by 400 % in the last 5 years. These seizures represent more than 25 % of the total MDMA seized in the European Community . An important aid in combating trafficking in illegal drugs is the ability to link seizures made at different times or locations to their common clandestine origin.



An interesting intrinsic parameter of the seized material is the natural abundance stable isotopic composition of the chemicals it contains. The $^{13}C/^{12}C$ and $^{15}N/^{14}N$ isotope ratios found in these chemicals directly depend on the physical and chemical environment from which they are derived. These parameters have proved valuable in characterising natural products, in which they are determined by environmental and metabolic factors, notably in relating products with different geographical and botanical features of their origin.

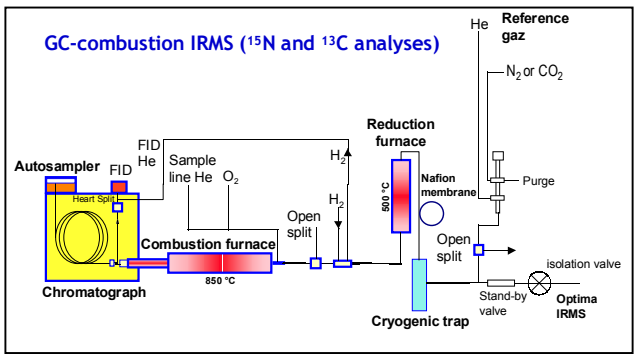
Contrary to illicit drugs derived from plant extracts, isotopic measurements can not provide information on geographical origin for synthetic drugs. In this case, isotopic ratios might be expected to depend on both precursors and synthetic route used.

In this study we have investigated the potential of $^{15}N/^{14}N$ isotope ratios to establish links between seizures of MDMA tablets, using continuous-flow GC-C-IRMS. It is shown that $^{15}N/^{14}N$ ratios could be used as an important additional parameter. This data can be useful for tracing the routes by which illicit drugs have arrived from their common origin.

Isotopic analyses

This study were performed on 35 samples for $\delta^{13}C$ measurements and 106 samples for $\delta^{15}N$ measurements. Tablets analysed are randomly chosen and representative of seizures made by French Customs between 1999 and 2002.

MDMA was analysed after liquid-liquid extraction. Efficiency of the extraction was ensured by GC-MS, and the absence of isotopic fractionation during this process was controlled by triplicate extraction of large sets of homogeneous samples.



^{15}N and ^{13}C analyses were performed by using a Fisons GC 8000 gas chromatograph interfaced to a Micromass Isochrom isotope ratio mass spectrometer. In addition to the classical system, these analyses required the fitting of a reduction furnace in order to reduce nitrogen oxydes. A Nafion membrane evacuates water on line and a cold trap at liquid nitrogen temperature is used to stop CO_2 during ^{15}N analyses.

Results

$\delta^{13}C$ values obtained by analysis of 35 samples vary between -24 and -28 ‰, typical for natural products derived from terrestrial vegetation. MDMA and many other designer drugs have in common the use of essential oils or natural products as starting materials. Thus, as ten of the eleven carbon atoms of MDMA can be supplied by safrole or isosafrole, coming from sassafras oil, the ^{13}C content of MDMA is expected to be close to the ^{13}C content of the precursors. This was verified by measurement of the ^{13}C content of several batches of precursors. These precursors, obtained from different suppliers range between -25 and -28 ‰. The weak variation observed for MDMA samples do not allow any linking of seized materials.

Nitrogen isotopic measurements were performed for 106 MDMA samples extracted from tablets coming from different seizures. $\delta^{15}N$ values obtained range between -17 and +18 ‰ with a very high dispersion. For each sample, standard deviation of the three injections was lower than 0,300 ‰. By comparison of these values, five groups of MDMA samples can be build up.

Nitrogenous precursors have also been analysed and ranged between -5 and +5 ‰. This small range of variation in $\delta^{15}N$ is insufficient to explain the larger range observed in the MDMA samples. So we can suppose that isotopic fractionation occurs during the synthetic process. In order to prove the presence of such a fractionation, many syntheses of different types were realised. Results of observed fractionation are presented in Figure 1.

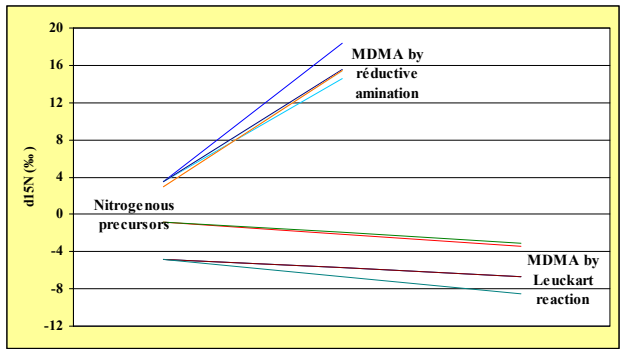


Figure 1 : *Isotopic fractionation observed after MDMA synthesis*

Reductive amination and Leuckart reaction are the most commonly used MDMA manufacturing processes in European clandestine laboratories. After these syntheses, specific and repeatable isotopic fractionation were noticed. These fractionations can explain the values observed for the two most populated groups of MDMA samples. Further study is actually conduct with other common synthetic routes to explain other $\delta^{15}N$ values obtained in seized materials.

Seizures comparison

Due to the lack of discrimination shown by the $\delta^{13}C$ values by itself and because comparison versus $\delta^{15}N$ values gives no additional information, only $\delta^{15}N$ results were used for the comparison of MDMA tablets. This comparison were performed by statistical analysis. Many samples can be linked by using $\delta^{15}N$ as additional parameter. Other parameters were physical features and MDMA content.

The statistical study was done by coupling Principal Component & Classification Analysis (PCCA) and Hierarchical Cluster Analysis (HCA). Figure 2 shows the dendrogram obtained by this way. The similarity index allow many MDMA samples to be linked, some of them with more than 95 % of similarity. Such samples were also compared by profiling analyses and results of statistical comparison were confirmed.

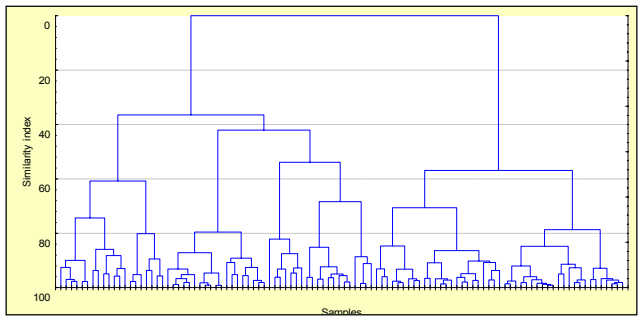


Figure 2 : Dendrogram resulting from the hierarchical cluster analysis of MDMA tablets

Conclusions

The aim of this study was to show the potential of GC-C-IRMS analyses to distinguish between different sources of synthetic drugs. The technique has been evaluated in particular for the determination of $\delta^{15}N$ variation in seized samples of MDMA. The results obtained show that such measurements can be an important parameter for the comparison of different samples. The ^{15}N isotopic ratio is a discriminating factor and can be an aid in linking different seizures.

However, isotopic discrimination between MDMA samples will also depend on the nitrogenous precursor used and on manufacturing process which can induce characteristic variations in the $\delta^{15}N$. In combination, these factors can explain the large range of measured $\delta^{15}N$ values.

This technique now needs to be refined through a systematic study of the influence of MDMA synthetic conditions on isotopic fractionation and completed by the constitution of a large database of $\delta^{15}N$ values for MDMA and potential precursors. In addition to qualitative and quantitative classical analyses, this should improve the identification and the comparison of manufacturing process and precursors, making it more feasible to link different samples seized in different places and at different times to a common origin.