Thermal Desorption Direct Analysis in Real Time Mass Spectrometry (TD-DART-MS) of Seized Drug Mixtures

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ABSTRACT

Direct analysis in real time mass spectrometry (DART-MS) can enable more effective screening of seized drug evidence. However, the presence of multiple components can lead to competitive ionization and requires complex mixture interpretation. This study explores thermal desorption (TD)-DART-MS to enhance the separation of mixture components and reduce concerns with competitive ionization and complex data interpretation.

INTRODUCTION

Seized drug analysis is the most frequently requested service from forensic science service providers across the United States, accounting for nearly a third of all requests [1]. Recently, DART-MS has gained popularity as a rapid seized drug screening method. DART-MS enables the rapid analysis of seized drug mixtures with little to no sample preparation; however, the presence of multiple components can lead to issues with sensitivity due to competitive ionization and requires complex mixture interpretation [2]. The incorporation of thermal desorption before DART-MS analysis provides a temperature-based separation to improve analyte detection and the ease of compound identification due to reduced competitive ionization and the production of single-component mass spectra.

In this study, a TD-DART-MS method was developed and validated for the analysis of commonly encountered seized drug mixtures. All analyses were completed using both helium and nitrogen as the DART source gas to assess the impact of source gas selection. The validation studies included selectivity, limit of detection, repeatability, and reproducibility. Providing the seized drug community with a validated TD-DART-MS method for rapid seized drug screening and an assessment of the impact of different source gases provides forensic laboratories with an additional resource to address the rapid screening of seized drug evidence.

MATERIALS & METHODS

Chemical and Materials

The compounds analyzed in this study include methamphetamine, cocaine, fentanyl, heroin, oxycodone, xylazine, procaine, caffeine, levamisole, acetaminophen, aniline, and dimethyl sulfone.

Sample Preparation

All pure samples used for the validation studies were prepared and analyzed as 10 ppm solutions. Twelve simulant mixtures were prepared combining two or three target compounds in 1:1 ratios at a concentration of 10 ppm per compound.

Sample Introduction

A 3 µL aliquot of each sample was pipetted into the center of a copper pot and allowed to dry. The copper pot was then placed into the ionRocket thermal desorption unit. Each sample was inserted under the glass tee junction at 0.4 minutes and the temperature program was started at 0.5 minutes.

RESULTS & DISCUSSION
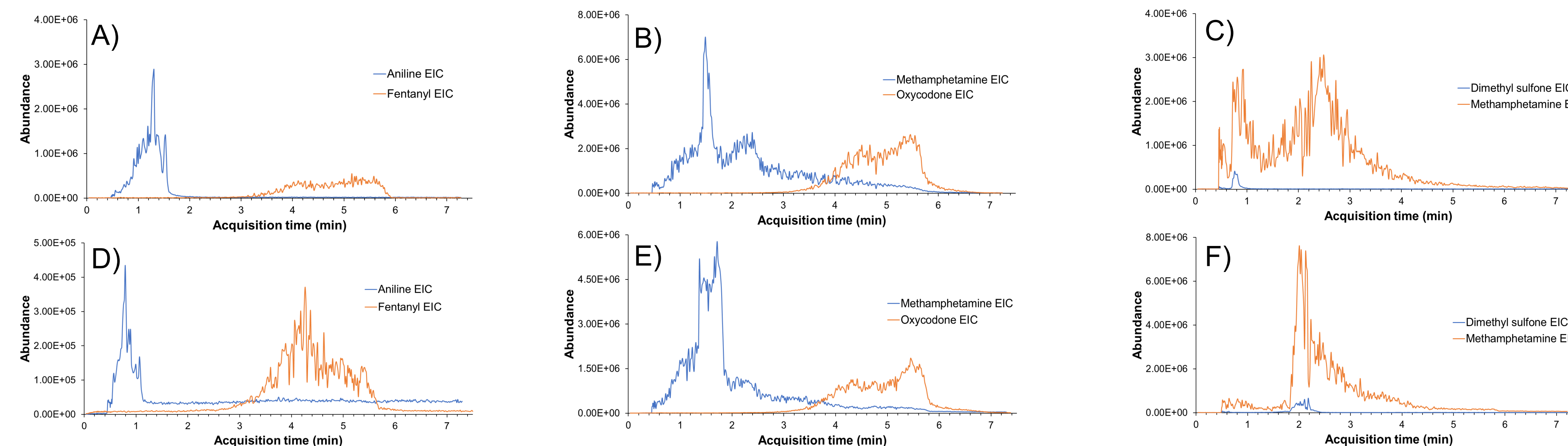
Figure 1. Extracted ion chronograms (EICs) for helium TD-DART-MS of A) aniline and fentanyl, B) methamphetamine and oxycodone, C) dimethyl sulfone and methamphetamine and for nitrogen TD-DART-MS of D) aniline and fentanyl, E) methamphetamine and oxycodone, and F) dimethyl sulfone and methamphetamine at 10 ppm.

- Several mixtures produced sufficient separation to produce single-component mass spectra.
- Overlapping compounds can still be identified individually; however, ionization suppression was observed in some cases.

Table 1. LOD for each compound using both source gases.

Compounds	Helium	Nitrogen
Methamphetamine	0.1 ppm	0.1 ppm
Cocaine	0.5 ppm	0.1 ppm
Heroin	0.5 ppm	0.5 ppm
Fentanyl	10 ppm	10 ppm
Oxycodone	5 ppm	1 ppm
Xylazine	5 ppm	0.5 ppm
Aniline	1 ppm	1 ppm
Dimethyl Sulfone	10 ppm	10 ppm
Procaine	0.5 ppm	0.5 ppm
Levamisole	0.5 ppm	0.5 ppm
Caffeine	0.5 ppm	0.5 ppm
Phenacetin	0.5 ppm	0.5 ppm
Acetaminophen	10 ppm	10 ppm
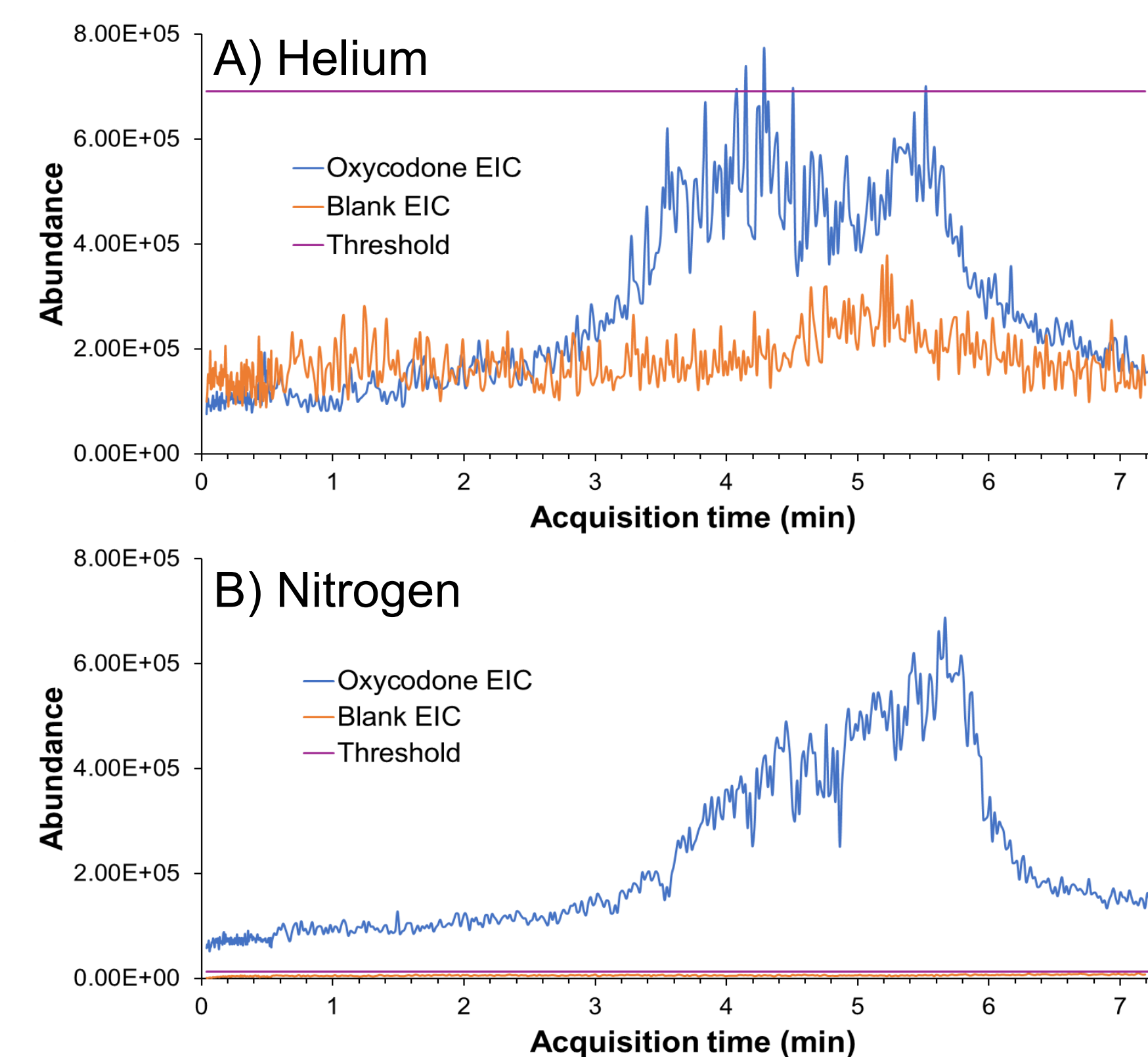
Figure 2. EIC of oxycodone at 0.5 ppm for A) helium and B) nitrogen.

- Nitrogen has a lower ionization efficiency than helium, enabling improved signal-to-noise ratios.
- Ionization enhancement in mixtures enabled several compounds to have improved LODs compared to the pure substance.
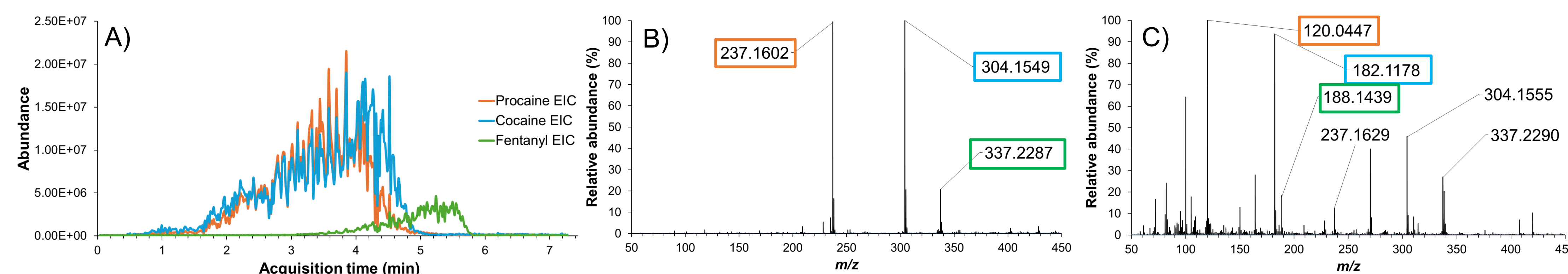
Figure 3. A) EIC of procaine, cocaine, and fentanyl and AIF data collected at B) 0 eV and C) 30 eV.

- AIF data enables compound identification utilizing the NIST DIT based on the presence of precursor and fragment ions.
- All controlled substances above the method LODs were identified in the blind simulant samples.
- Acetaminophen and dimethyl sulfone were not correctly identified, likely due to competitive ionization and higher LODs.
- Potential carryover was observed for phenacetin and caffeine in two blind simulant samples.

MATERIALS & METHODS

Instrumentation

An ionRocket thermal desorption unit was coupled with an IonSense DART JumpShot® ionization source and an Agilent 6530 quadrupole time-of-flight mass spectrometer for analysis of the seized drug mixtures. The thermal desorption temperature program included a 0.8-minute hold at 40 °C followed by a 30 °C/minute ramp rate to 200 °C with an additional 0.5-minute hold for a total analysis time of 6.6 minutes. All TD-DART-MS data was collected in positive ionization mode with a scan range of *m/z* 50-450. All ion fragmentation (AIF) acquisition mode was used to obtain low, medium, and high fragmentation spectra at collision energies of 0 eV, 30 eV, and 60 eV.

Data Analysis

Mass spectral data was extracted as both profile and centroid data using MassHunter Qualitative Analysis and exported as .CSV files into Microsoft Excel. The profile data was background subtracted utilizing the background spectrum acquired when methanol was added to a blank copper pot. The background-subtracted profile data was then used for the validation studies.

CONCLUSIONS

❖ All controlled substances and cutting agents were identified using both helium and nitrogen as the DART source gas.
❖ The limit of detection was 10 ppm or less for all compounds.
❖ Nitrogen enabled lower limits of detection in some cases due to more selective ionization and reduced background noise.
❖ Mixture components that overlap are still identifiable in the AIF mass spectra, although ionization suppression was observed.
❖ Ionization enhancement was observed for fentanyl, methamphetamine, and oxycodone when analyzed in mixtures.
❖ Controlled substances identified in blind simulant mixtures.

REFERENCES

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[2] W. Dong, J. Liang, I. Barnett, P.C. Kline, E. Altman, M. Zhang, The classification of Cannabis hemp cultivars by thermal desorption direct analysis in real time mass spectrometry (TD-DART-MS) with chemometrics, Analytical and Bioanalytical Chemistry 411(30) (2019) 8133-8142.

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