Exploring the Ionization Space in Traditional Electron Ionization with High Resolution GC-TOFMS for a Variety of Compound Classes

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Introduction

Recommended source conditions for contributing electron ionization (EI) mass spectra to commercial libraries are ionization energy of 70 eV and an ion source temperature of 200°C. However, spectral quality is affected by other source parameters, such as filament emission current and differences in instrument manufacturers' source design.

- The primary objective of this study was to optimize LECO's GC-HRT EI source parameters to enhance the molecular ion of thermally labile compounds like linear alkanes, fatty acid methyl esters, and pesticides.
- The secondary objective was to optimize the EI source for other classes of compounds to achieve a global optimum for non-targeted analysis, since this is the primary utility of most time-of-flight mass spectrometry (TOFMS) systems.

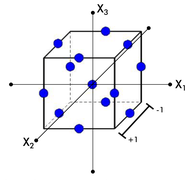
Methods

A mixture of standard solutions was prepared containing C_8-C_{40} alkanes, fatty acid methyl esters, pesticides, polycyclic aromatic hydrocarbons, as well as other classes of compounds; 80 compounds in total. The solution was analyzed using an Agilent 7693 autosampler and 7890 GC, coupled to a LECO Pegasus® GC-HRT.

- Electron energies were tested from 30 to 70 eV
- Filament emission current from 0.1 to 3.0 mA; normalized with filament current (A)
- Source temperature ranged from 200 to 300°C
- Outcomes were measured using LECO's ChromaTOF-HRT® software.

The objectives were evaluated using design-of-experiment (DoE) in XLSTAT.

Box-Behnken Design



Experimental design (Box-Behnken design):

Observation	Run order	Repetition	Source Temperature	Electron Energy	Filament Current
Obs1	1	1	200	30	2.75
Obs2	2	1	300	30	2.75
Obs3	3	1	200	70	2.75
Obs4	4	1	300	70	2.75
Obs5	5	1	200	50	2.6
Obs6	6	1	300	50	2.6
Obs7	7	1	200	50	2.9
Obs8	8	1	300	50	2.9
Obs9	9	1	250	30	2.6
Obs10	10	1	250	70	2.6
Obs11	11	1	250	30	2.9
Obs12	12	1	250	70	2.9
Obs13	13	1	250	50	2.75

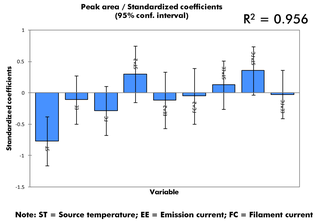
The design goals were to: (1) maximize molecular ion preservation as indicated by the molecular ion chromatographic peak area, (2) maximize the library similarity score, and (3) maintain chromatographic peak shape.

Optimal source conditions were determined from the equation of the models using SOLVER in Microsoft® Excel.

Eicosane (C_{20}-alkane)

Peak area was the most important outcome of the model.

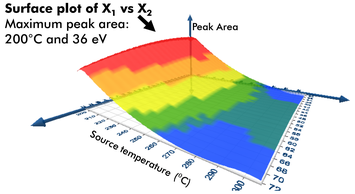
Equation of the model:
Peak area = 5208-7847.875*ST-1129.125*EE-2920.5*FC+4866.125*ST^2-1872.375*EE^2-847.6250*FC^2+1865.75*ST*EE+5144*ST*FC-363*EE*FC



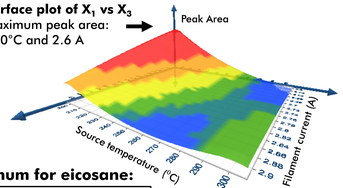
Note: ST = Source temperature; EE = Emission current; FC = Filament current

Source temperature was the most important variable to maximize sensitivity.

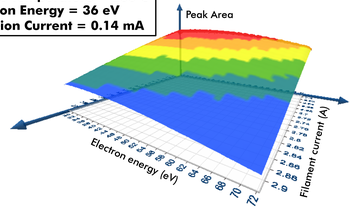
Surface plot of X_1 vs X_2
Maximum peak area:
200°C and 36 eV



Surface plot of X_1 vs X_3
Maximum peak area:
200°C and 2.6 A



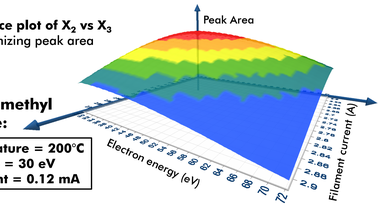
Optimum for eicosane:
Source Temperature = 200°C
Electron Energy = 36 eV
Emission Current = 0.14 mA



Methyl dodecanoate

For thermally labile compounds such as linear alkanes, fatty-acid methyl esters, and pesticides, source temperature was the most important variable, followed by electron energy and emission current.

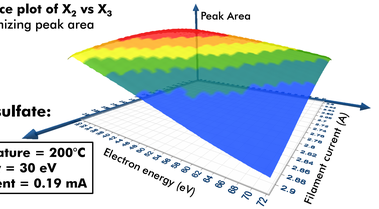
Surface plot of X_2 vs X_3
maximizing peak area



Optimum for methyl dodecanoate:
Source Temperature = 200°C
Electron Energy = 30 eV
Emission Current = 0.12 mA

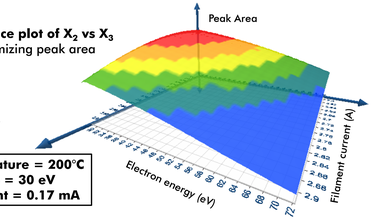
Pesticides

Surface plot of X_2 vs X_3
maximizing peak area



Optimum for endosulfan sulfate:
Source Temperature = 200°C
Electron Energy = 30 eV
Emission cCurrent = 0.19 mA

Surface plot of X_2 vs X_3
maximizing peak area

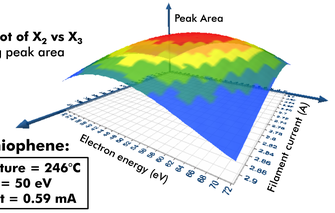


Optimum for dichlorvos:
Source Temperature = 200°C
Electron Energy = 30 eV
Emission Current = 0.17 mA

- Source temperature was set to 200°C for the surface plots of electron energy vs filament current (X_2 vs X_3), to maximize peak area using the equation of the model for each of the thermally labile compounds.
- Peak area and similarity score were positively correlated, so peak area was represented in the equation of the models only.
- Peak shape was not variable enough to develop a model.

Tetrabromothiophene

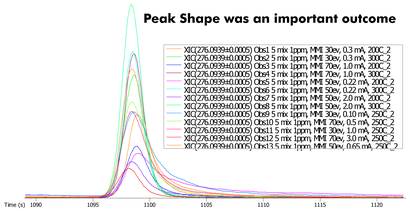
Surface plot of X_2 vs X_3
maximizing peak area



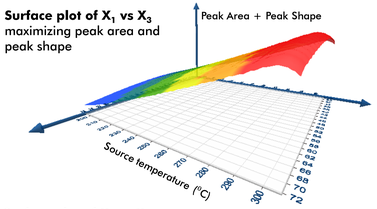
Optimum for tetrabromothiophene:
Source Temperature = 246°C
Electron Energy = 50 eV
Emission Current = 0.59 mA

Benzo[g,h,i]perylene

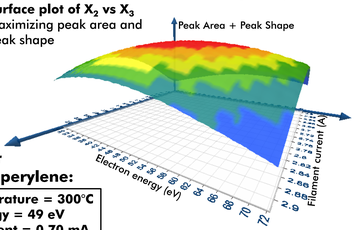
Peak Shape was an important outcome



Surface plot of X_1 vs X_3
maximizing peak area and peak shape



Surface plot of X_2 vs X_3
maximizing peak area and peak shape



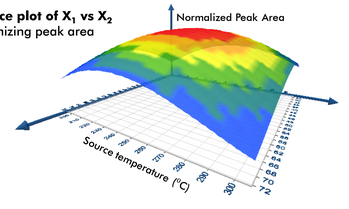
Optimum for benzo[g,h,i]perylene:
Source Temperature = 300°C
Electron Energy = 49 eV
Emission Current = 0.70 mA

Global Optimum

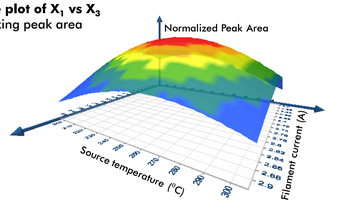
Global optimum considering normalized peak areas for 24 compounds.

- **Linear alkanes, FAMEs, phenols, PAHs, pesticides, amines, and halogenated aromatics.**

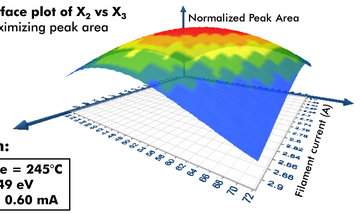
Surface plot of X_1 vs X_2
maximizing peak area



Surface plot of X_1 vs X_3
maximizing peak area



Surface plot of X_2 vs X_3
maximizing peak area



Global Optimum:
Source Temperature = 245°C
Electron Energy = 49 eV
Emission Current = 0.60 mA

Conclusion

- Source temperature was commonly the most significant variable for maximizing molecular ion peak area.
- Chromatographic peak shape was temperature dependant primarily for the non-volatile compounds.
- Ionization conditions were optimized to maximize molecular ion for a variety of compound classes.
- Ionization conditions do change the peak shape and peak area, which relates directly to library searchability.

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