

Gas Chromatography/Mass Spectrometry Analysis of Di-*n*-Octyl Disulfide in a Straight Oil Metalworking Fluid with Differential Permeation and Box-Cox Transformation

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Goal

- To identify and quantify an unknown in a complex mixture
 - D4
 - Metalworking fluid
 - NIOSH REL 0.4 mg/m³ (thoracic)



Specific Aims

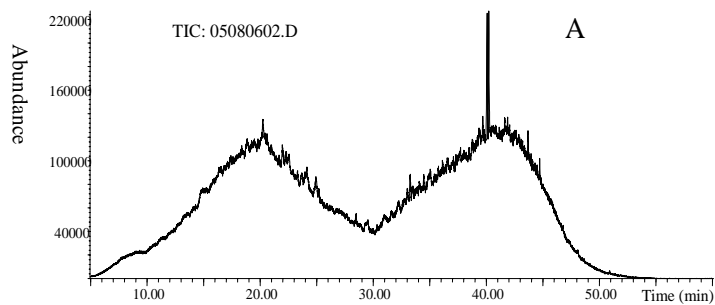
- To analyze a complex metalworking fluid with GC-MS
- To linearize the calibration curve with Box-Cox power transformation



GC-MS

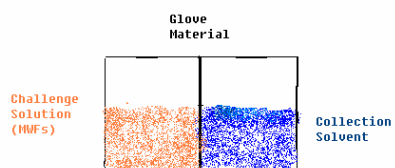
- GC as separator, and MS as detector
- Mode of MS
 - Selected ion monitoring (SIM)
 - Total ion current monitoring (TIC)
 - Extracted ion chromatogram (EIC)
- Quantification method
 - Internal standard
 - Standard additions

TIC-GC-MS of D4



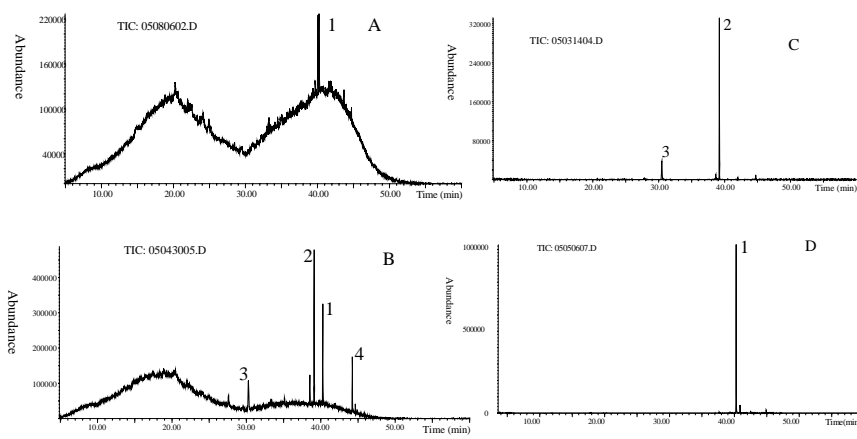
- Thousands of components in the two broad envelopes.

Permeation of D4

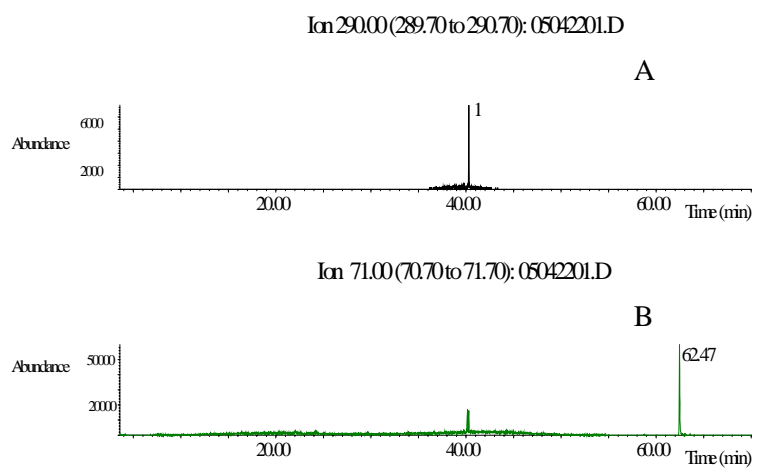


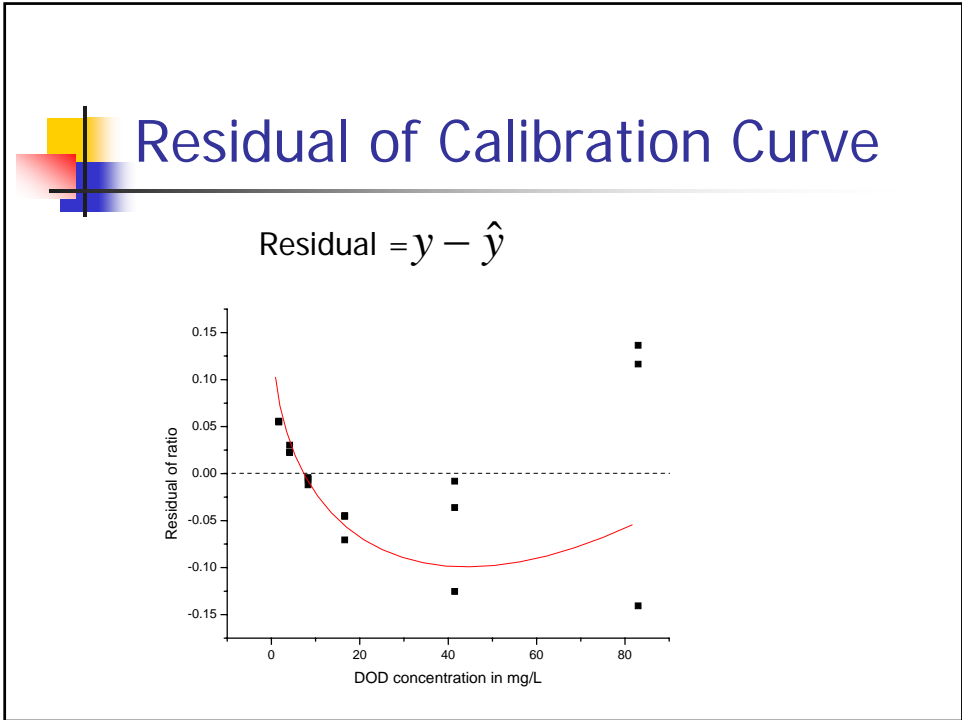
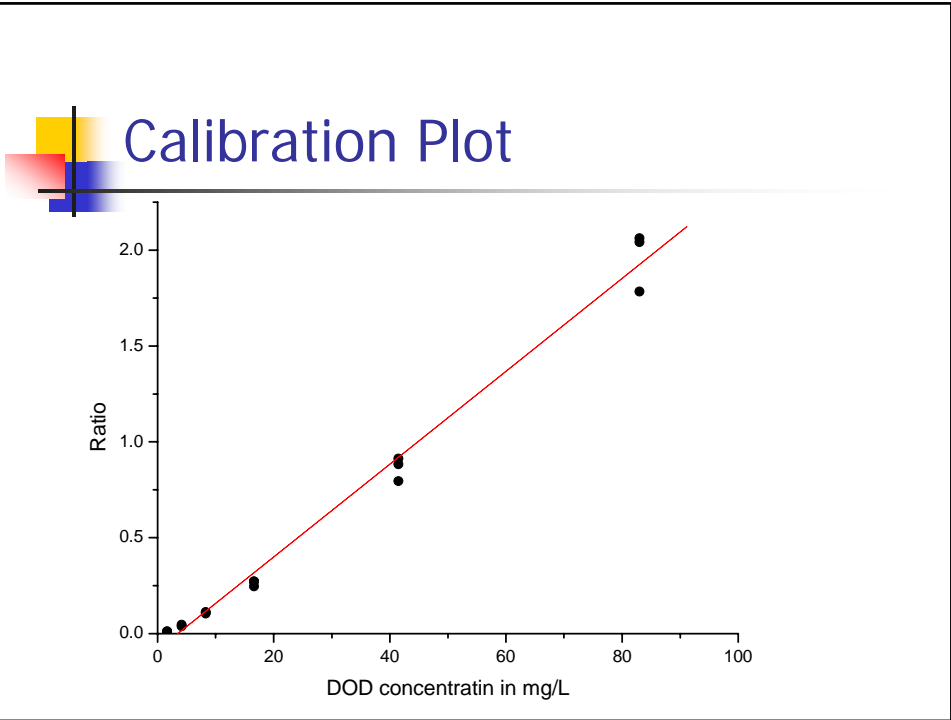
- ASTM permeation cell
- Thermostatted at 35°C

GC-MS of D4

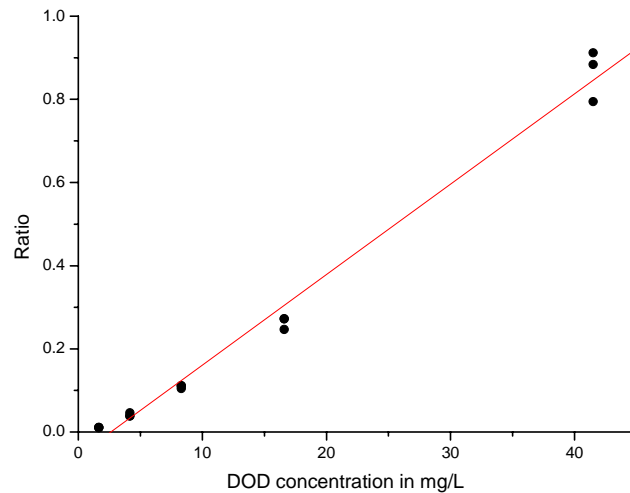


EIC of Original D4





Calibration Curve: Lower Concentrations

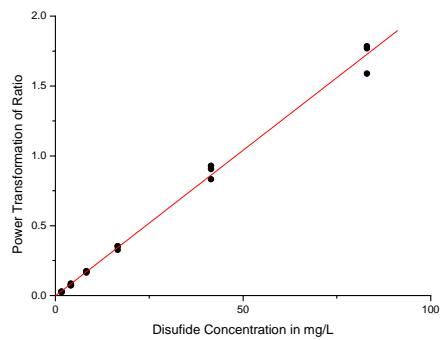
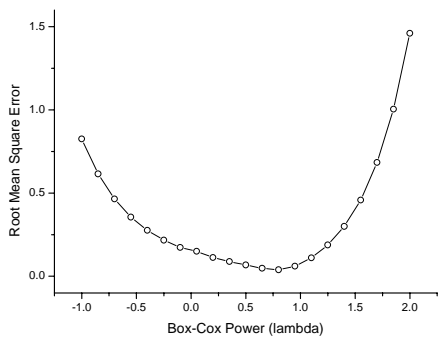


Box-Cox Transformation

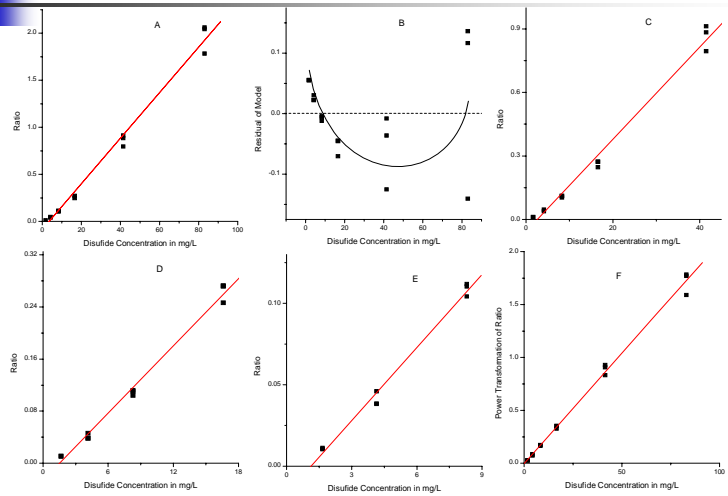
- General linear calibration: $y = a + bx$
- Transformation: $z = a + bx$, where $z = \ln y$, $y^{1/2}$, $y^2 \dots$
- Box-Cox transformation: $z = a + bx$, where
$$z = \frac{y^\lambda - 1}{\lambda} \text{ for } \lambda \neq 0 \text{ and } z = \ln y \text{ for } \lambda = 0$$
- SAS, STATA, R, SPSS

Box-Cox Transformation

$$\text{Root mean square error} = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n}}$$



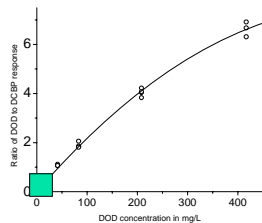
Calibration Curves



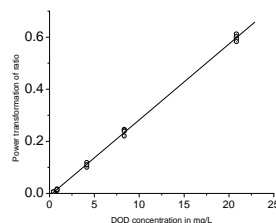
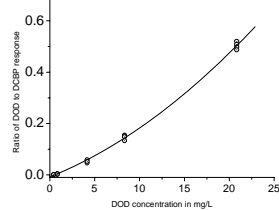
DOD in D4

- $0.398 \pm 0.034\%$ (w/w) by the internal standard method
- $0.387 \pm 0.036\%$ (w/w) by the method of standard additions using Box-Cox
- $0.293 \pm 0.046\%$ (w/w) by the method of standard additions without Box-Cox

Another Example of Box-Cox



- DOD
- Temperature program
- IS 4,4'-dichlorobiphenyl





Summary

- GC-MS was used to quantify DOD in a metalworking fluid
- Differential permeation helped the identification by minimizing MWF interference
- Box-Cox transformation is useful to linearize calibration curve for quantification



Acknowledgement

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Reference: Xu, W., and Que Hee, S. S. (2006). GC-MS Analysis of Di-*n*-Octyl Disulfide in a Straight Oil Metalworking Fluid: Application of Differential Permeation and Box-Cox Transformation. *Journal of Chromatography A*. 1101, 25-31.