

Identification of Sulfur Compounds in Petroleum Samples Using Derivatization with Mass

Deficient Reagents

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OVERVIEW

A novel approach for identification of sulfur (S)-containing compounds in complex mixtures (e.g., petroleum) based on the use of a selective mass deficient derivatizing reagent is introduced.

INTRODUCTION

The complete molecular characterization of petroleum samples remains a challenge, due to the complexity of these samples. The molecular characterization is important in optimization of refinery processes in the petroleum industry to help reduce emission of toxic gases from combustion of heteroatom (N, O, and S)-containing compounds [1]. Ultrahigh resolution mass spectra of petroleum samples reveal the presence of multiple peaks at each nominal mass and Kendrick plots are often used to simplify the interpretation of these petroleum mass spectra [2].

Our goal is to use a mass deficient derivatizing reagent for selective tagging of S-containing compounds in complex samples. Tagged S-containing compounds are subsequently detected by MS and Kendrick plot analysis.

METHODS

Samples: Acetophenone, aniline, benzaldehyde, 1-(bromomethyl)-2,3,4,5,6-pentafluorobenzene (1-BMP), methanol, thiophenol were purchased from Sigma (Sigma-Aldrich, St. Louis, MO). Hydrogen peroxide and triethylamine were purchased from Acros (Acros Organics, Fair Lawn, NJ). Acetic acid and dichloromethane were purchased from EMD (EMD Serono, Inc., Billerica, MA). Benzoic acid was purchased from Mallinckrodt (Mallinckrodt, St. Louis, MO). Phenol was purchased from Fisher (Fisher Scientific, Pittsburgh, PA).

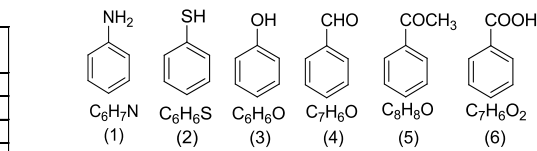
Instrumentation: Mass spectra were acquired using a Thermo LTQ/Orbitrap mass spectrometer (Thermo Fisher Scientific, Waltham, MA) equipped with an atmospheric pressure chemical ionization (APCI) source. Mass spectra in both positive- and negative-ion modes were acquired to maximize analyte coverage. Typical APCI conditions were as follows: vaporizer temperature, 360 °C; sheath gas flow rate, 12 arbitrary units (AUs); auxiliary gas flow rate, 8 AUs; discharge current, 0.5 μA; capillary temperature, 180 °C; transfer capillary voltage, 10 V; tube lens, 15 V. All experiments, including chemical reaction trials and MS acquisitions, were conducted in triplicate to ensure reproducibility.

RESULTS

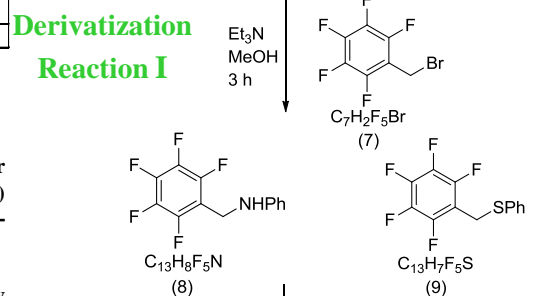
(I) Derivatization Reactions

Table 1. List of the chemical compounds used in our standard mixture. **Standard Mixture of 6 Analytes**

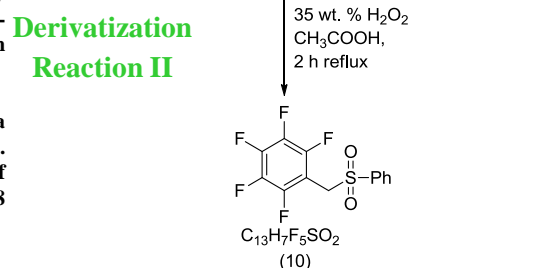
Compounds	Molecular Weight (g/mol)	Density (g/mL)	Added Volume (mL)	Added Mass (g)
Aniline	93.12648	1.022	0.09	NA
Acetophenone	120.14852	1.030	0.12	NA
Benzaldehyde	106.12194	1.045	0.10	NA
Benzoic acid	122.12134	1.320	NA	0.1232
Phenol	94.11124	1.071	NA	0.0951
Thiophenol	110.17684	1.073	0.10	NA



Derivatization Reaction I



Derivatization Reaction II



Scheme 1. Derivatization reaction scheme used for selective tagging of thiophenol (a S-containing compound) using 1-(bromomethyl)-2,3,4,5,6-pentafluorobenzene (1-BMP) as a selective mass deficient derivatizing reagent.

In reaction I, both N- and S-containing compounds may react with 1-BMP. However, in reaction II, only S-containing compound undergoes a selective oxidation reaction with hydrogen peroxide (H₂O₂).

The reaction II product (10) can then be detected as a protonated species using APCI/MS in positive ion-mode. The final product (10) has a Kendrick mass defect of 0.34471 (as compared to Kendrick mass defect of 0.10998 for the initial S-containing compound (2)).

(II) APCI Mass Spectra of the Standard Mixture (Before any Derivatization) (Positive- and Negative-Ion Modes)

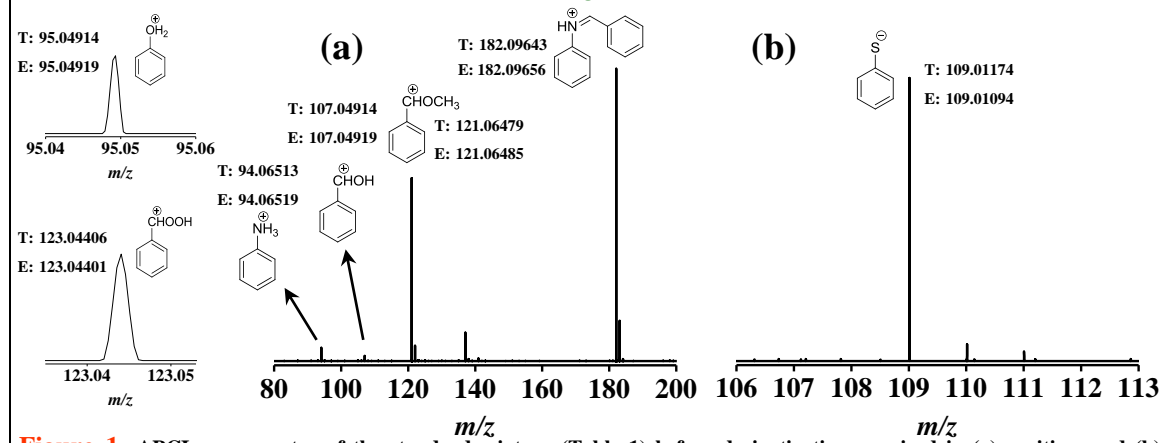


Figure 1. APCI mass spectra of the standard mixture (Table 1) before derivatization acquired in (a) positive- and (b) negative-ion modes. Insets in panel (a) show expanded views of *m/z* ranges from 95.040 to 95.060 (top) and 123.035 to 123.053 (bottom) corresponding to protonated phenol and benzoic acid, respectively.

[Note: In positive-ion mode, all of the components in the standard mixture, except thiophenol, were observed. In negative-ion mode, only deprotonated thiophenol was observed.]

(III) APCI Mass Spectrum of the Standard Mixture (After the Derivatization Reaction I)

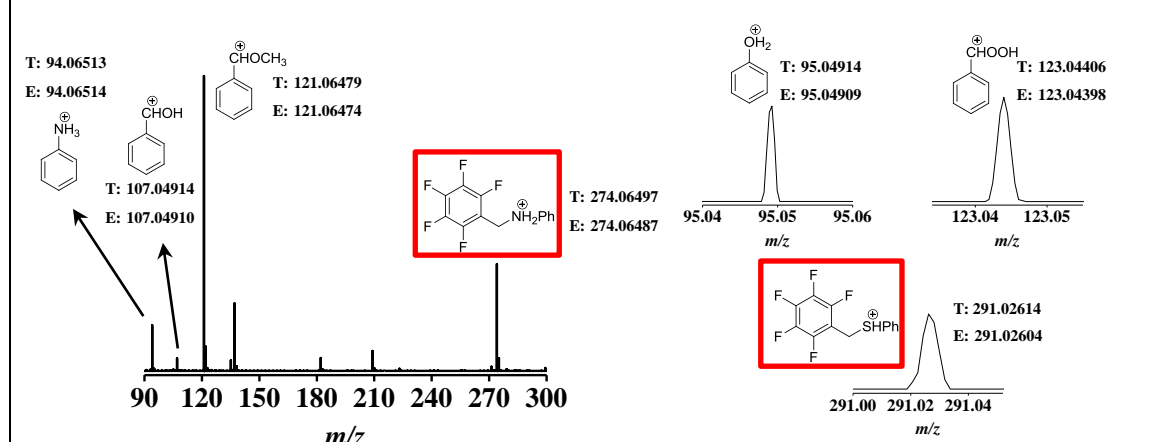


Figure 2. Positive-ion mode APCI mass spectrum of the standard mixture (Table 1) after the derivatization reaction I (Scheme 1). Insets (right panels) show expanded views for *m/z* ranges from 95.040 to 95.060 (top left), 123.034 to 123.055 (top right) and 291.000 to 291.052 (bottom), corresponding to protonated phenol, protonated benzoic acid, and protonated ((perfluorophenyl)methyl)(phenyl)sulfane, respectively.

[Note: derivatized products from aniline and thiophenol are shown within red boxes.]

(IV) APCI Mass Spectrum of the Standard Mixture (After the Derivatization Reaction II)

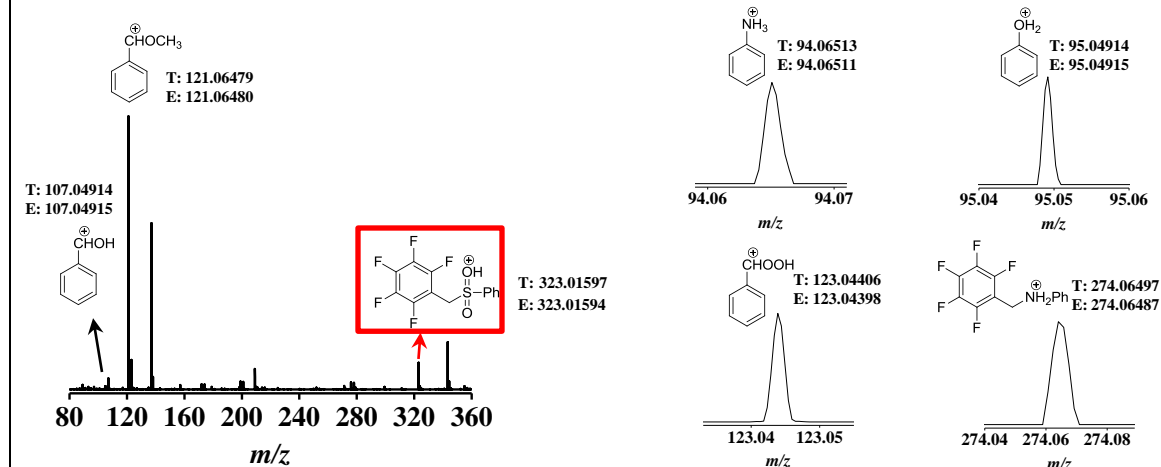


Figure 3. Positive-ion mode APCI mass spectrum of the standard mixture (Table 1) after derivatization reaction II (Scheme 1). Insets show expanded views for *m/z* ranges from 94.059 to 94.071 (top left), 95.040 to 95.060 (top right), 123.033 to 123.055 (bottom left), and 274.040 to 274.089 (bottom right) corresponding to protonated aniline, phenol, benzoic acid, and N-(perfluorophenyl)methylaniline, respectively.

[Note: mass spectrum in Fig 3. shows the presence of a reaction II product for thiophenol (a S-containing compound) (shown within a red box.)]

(V) Kendrick Mass Defect vs Nominal Kendrick Mass for all Standard Mixtures

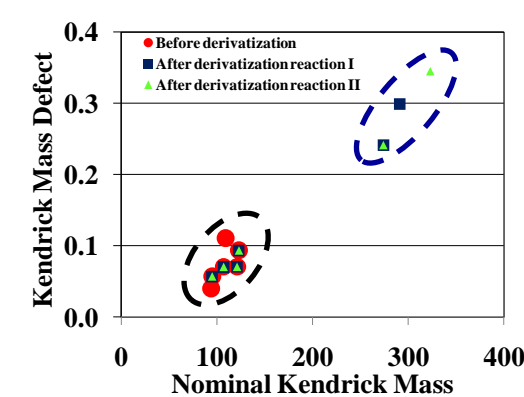


Figure 4. Plot of Kendrick mass defect versus nominal Kendrick mass obtained after Kendrick mass analyses of Figures 1, 2, and 3.

(Note the increase in Kendrick mass defects of the initial standard compounds (shown within the black dash ellipsoid) after derivatization reactions (shown within the blue dash ellipsoid). This approach allows for detection and differentiation of both nitrogen- and sulfur-containing compounds present in complex mixtures.)

In this example, side reactions are limited (viz., reaction of two original analytes to yield a neutral product that corresponds to an ion at *m/z* 182.09656 (Fig. 1a)). However, for more complex crude oil and petroleum samples additional unwanted side reactions may limit the applicability of the presented approach.)

Table 2. Summary of the measured and exact masses for all standard mixture components before and after the derivatization reactions I and II.

Chemical Formula	Theoretical <i>m/z</i>	Before Derivatization					Kendrick mass defect	Mass accuracy (ppm)	Kendrick mass defect error
		Theoretical nominal Kendrick mass	Theoretical Kendrick mass defect	Measured <i>m/z</i>	Nominal Kendrick mass	Measured Kendrick mass			
C ₆ H ₆ S ⁺	109.01174	109	0.10998	109.01094	109	0.11078	-7.3	8.0E-04	
C ₆ H ₆ O ⁺	95.04914	95	0.05699	95.04919	95	0.05694	0.53	-5.0E-05	
C ₆ H ₇ N ⁺	94.06513	94	0.03990	94.06519	94	0.03984	0.64	-6.0E-05	
C ₇ H ₆ O ₂ ⁺	123.04406	123	0.09333	123.04401	123	0.09338	-0.41	5.0E-05	
C ₇ H ₆ O ⁺	107.04914	107	0.07039	107.04919	107	0.07034	0.47	-5.0E-05	
C ₈ H ₈ O ⁺	121.06479	121	0.07039	121.06485	121	0.07033	0.50	-6.0E-05	
After Derivatization Reaction I									
C ₁₃ H ₆ F ₅ S ⁺	291.02614	291	0.29882	291.02604	291	0.29892	-0.34	1.0E-04	
C ₆ H ₆ O ⁺	95.04914	95	0.05699	95.04909	95	0.05704	-0.53	5.0E-05	
C ₁₃ H ₆ F ₅ N ⁺	274.06497	274	0.24105	274.06487	274	0.24115	-0.36	1.0E-04	
C ₇ H ₆ O ₂ ⁺	123.04406	123	0.09333	123.04398	123	0.09341	-0.65	8.0E-05	
C ₇ H ₆ O ⁺	107.04914	107	0.07039	107.04910	107	0.07043	-0.37	4.0E-05	
C ₈ H ₈ O ⁺	121.06479	121	0.07039	121.06474	121	0.07044	-0.41	5.0E-05	
After Derivatization Reaction II									
C ₁₃ H ₆ F ₅ O ₂ S ⁺	323.01597	323	0.34471	323.01594	323	0.34474	-0.09	3.0E-05	
C ₆ H ₆ O ⁺	95.04914	95	0.05699	95.04915	95	0.05698	0.10	-1.0E-05	
C ₁₃ H ₆ F ₅ N ⁺	274.06497	274	0.24105	274.06487	274	0.24115	-0.36	1.0E-04	
C ₇ H ₆ O ₂ ⁺	123.04406	123	0.09333	123.04398	123	0.09341	-0.65	8.0E-05	
C ₇ H ₆ O ⁺	107.04914	107	0.07039	107.04915	107	0.07038	0.09	-1.0E-05	
C ₈ H ₈ O ⁺	121.06479	121	0.07039	121.06480	121	0.07038	0.08	-1.0E-05	

CONCLUSIONS

• We demonstrated the utility of mass deficient tagging and showed experimental results from this novel approach for identification of sulfur-containing compounds in standard sample mixtures.

• Using 1-(bromomethyl)-2,3,4,5,6-pentafluorobenzene (1-BMP) as a mass deficient derivatizing reagent, we showed 0.23473 increase in Kendrick mass deficiency for thiophenol (an S-containing compound).

• The approach presented here can be used to simplify the interpretation of Kendrick plots obtained from complex sample mixtures and rapidly identify S-containing compounds in the mixture.

REFERENCES

- [1] Alan G. Marshall, Ryan P. Rodgers, *Proceedings of the National Academy of Sciences*, 2008, 105, 18090–18095.
- [2] Christine A. Hughey, Christopher L. Hendrickson, Ryan P. Rodgers, Alan G. Marshall, *Anal. Chem.*, 2001, 73, 4676-4681.
- [3] Song, Jianglei. Dissertation, Baylor University, 2012.

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