



# ThP05 Biogenesis of Volatile Selenium Compounds in a Biomass/Biofuel Material and Quantification by VD-GC-ICP-MS

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## 1. ABSTRACT

A study of the transformation of selenium in broiler chicken litter (biomass feedstock) is being conducted using vacuum distillation-gas chromatography-inductively coupled plasma-mass spectrometry (VD-GC-ICP-MS). Early experiments indicate that the essential trace element is susceptible to biomethylation in the litter during incubation or fermentation. Dimethyl selenide (DMSe), dimethyl diselenide (DMDSe), and dimethyl selenenyl sulfide (DMSSeS) are the major volatile selenium species biogenerated in the samples during incubation.

## 2. INTRODUCTION

Increase in fuel costs and the need for cleaner or green energy have intensified the search for alternative energy sources other than fossil fuels. Biomass "plant and plant-derived material or animal waste that can be converted into fuels", has received a lot of attention as an alternative to fossil fuels. Currently, corn grain is used to produce the vast majority of ethanol in the United States; however there is a great potential that cellulose and hemicellulose will gain popularity in the future.

One of the current biomass feedstocks generating interest is poultry litter from concentrated animal feedlot operations (CAFOs). The material is available in large quantity, it contains wood shavings, corn and other grains and is; therefore, highly suitable for lignocellulosic liquid biofuels production. Poultry litter is rich in nitrogen, sulfur, and trace minerals including the essential trace-element selenium (Se). There is concern that the emission of nitrogen, sulfur and trace-elements derivatives during the fermentation and combustion of poultry litter need to be addressed.

A pilot study is being conducted, with particular emphasis on emission products of trace elements, using broiler chicken litter as biomass. Preliminary results for selenium, using the novel analytical approach of VD-GC-ICP-MS for the on-line extraction and quantification of the Se analytes from the sample matrix, are presented in this poster.

## 3. EXPERIMENTAL

Table 1. Selenium compounds and SW-846 Method 8261A [1] internal standards used in the study.

Compound	CAS No.	Boiling point (°C)	Relative volatility	Monitored Ions	Retention time (min)
Dimethyl selenide (DMSe)	593-79-3	52.8	14.3	82 and 78	10.54
Diethyl selenide (DESe)	627-53-2	108	11.9	82 and 78	15.61
Dimethyl diselenide (DMDSe)	7101-31-7	155-157	15.4	82 and 78	20.96
Vinyl chloride-d <sub>3</sub>	6745-35-3	-13.4	0.48	35 and 37	6.21
Methylene chloride-d <sub>2</sub>	1665-0-5	40	11.1	35 and 37	9.51
1,2-Dichloroethane-d <sub>4</sub>	107-06-2	84	20	35 and 37	12.49
1,2-Dichloropropane-d <sub>5</sub>	93952-08-0	95	11	35 and 37	13.71
1,1,2-Trichloroethane-d <sub>3</sub>	171086-93-4	112	26.6	35 and 37	16.49
1,2-Dibromomethane-d <sub>4</sub>	22581-63-1	131	26	79 and 81	17.95
Chlorobenzene-d <sub>5</sub>	3114-55-4	131	6.27	35 and 37	18.96
4-Bromofluorobenzene	460-00-4	152	8.05	79 and 81	21.69
Bromobenzene-d <sub>5</sub>	4165-57-5	155	7.93	79 and 81	21.97
1,2,-Dichlorobenzene-d <sub>4</sub>	95-50-1	180	7.86	35 and 37	24.02
1,2,4-trichlorobenzene-d <sub>3</sub>	2199-72-6	213	7.88	35 and 37	25.95
1,2,3-Trichlorobenzene-d <sub>3</sub>	3907-98-0	218.5	12	35 and 37	26.61

Calibration standards (1, 5, 10, 50, 100 and 250 ng as Se) were prepared in 5-mL reagent water (nitrogen-purged deionized water). The internal standards solution was prepared as recommended in EPA SW-846 Method 8261A.

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Figure 1. VD-GC-ICPMS Instrumentation

### Incubation Experiment

Litter from broiler chickens fed with a standard diet containing selenium was used. The total concentration of selenium in the dried litter was determined to be 1.2 mg/kg by ICP-MS. Aliquots of milled broiler litter (2 g) were weighed to 0.001 g into 100-mL round-bottomed VD flasks and 10 mL of reagent water was added. The flasks were sealed (O-ring caps) and the contents were mixed with a magnetic stirrer for two minutes. The vessel assemblies were then covered with aluminum foil and the moist litter samples were allowed to incubate at room temperature. A total of eight samples were prepared. Duplicate samples were analyzed at intervals of 0, 2, 8 and 30 days. When ready for analysis, the incubation flask was attached to a VD port. Each sample was spiked with a 5 µL aliquot of the internal standards solution and the slurry mixed for 5 minutes with the aid of a magnetic bar. Analyte extraction and quantification was performed using the VD-GC-ICP-MS analytical system shown in Figure 1.

### VD-GC-ICP-MS Analytical System and Operating Conditions

A 12-port vacuum distiller/concentrator (Cincinnati Analytical Instruments Model VDC1012 vacuum distiller, Indianapolis, IN) was used to extract the selenium analytes from the sample matrix. Specially designed VD vessels with side arm injection port (TG-Scientific Glass, Laguna Hills, CA) facilitated the introduction of internal standards into the samples. A heated transfer line transported the analytes contained in vacuum distillates to a GC (Agilent 6980N) equipped with a Gerstel injector and fitted with a capillary column (30 m x 0.25-mm i.d., 1.5-µm film VOCOL, Supelco, Bellefonte, PA). The separated species were entrained in a stream of helium and argon, via another heated sample transfer line, into the ICPMS (Agilent 7500 CX, Agilent Technologies, Palo Alto, CA).

Samples were vacuum distilled for 7.5 min with a 2.5 min transfer to the GC-ICP-MS. The VD and the GC transfer lines were held at 200 and 220°C, respectively. The temperature of the Gerstel injector was maintained at 200°C. The GC operating conditions were 2.5 min at -20°C, 40°C/min ramp to 60°C, 5°C/min ramp to 120°C and held for 1 min, 20°C/min ramp to 220°C and held for 12 min, resulting in a GC run time of 34 min. The injection was split 20:1 with a constant helium flow rate of 1.0 mL/min. The ICPMS operating conditions included plasma gas flow at 14.7 L/min, auxiliary gas at 0.9 L/min, carrier gas at 0.85 L/min, and forward power at 600 watts. The ICP-MS was tuned using 1% (v/v) xenon in helium at 1 mL/min. The chromatographic data were acquired using the Agilent ChemStation software in time-resolved analysis (TRA) mode with 100-msec dwell time for each element monitored.

## 4. RESULTS AND DISCUSSION

- The VD-GC-ICP-MS method was optimized for dimethyl selenide, dimethyl diselenide and diethyl selenide. Analyte quantification was performed following SW-846 Method 8261A (VD-GC-MS) which uses a suite of volatile organic internal standards to measure and adjust recoveries impacted by the matrix effects expected from biomass and biosolids (relative to compounds' boiling points and relative volatilities). The Br and Cl internal standards (Table 1) used in this study have boiling points or relative volatilities that bracket the range for the selenide compounds.
- The calibration standard deviations were all below 10% (5 to 250 ng for DMSe and DESe and 25 to 250 ng for DMDSe). The limit of quantification for this set of analyses was 2.5 ppb while the amount detected by ICPMS was <30 ppt reflecting a 20:1 injector split. Dimethyl diselenide, which has a higher boiling point (Table 1), was not as efficiently distilled out of the aqueous solution which in part explained a 5 fold increase in limit of detection. The chromatogram of a 100 ng (as Se) of the target selenide compounds is shown in Figure 2. The DMDSe standard contained a small amount of DMSes which appeared in the chromatogram at 18.38 min. The identity of DMSes was confirmed by VD-GC-MS.
- The incubation experiment was conducted as described in Section 3. Dimethyl selenenyl sulfide, was the predominant volatile selenium compound identified in the 48-h incubation samples followed by dimethyl selenide. In addition to DMSes, the 48-h litter samples produced other sulfur containing species including methanethiol (MSH) and dimethyl disulfide (DMDS).
- DMSe was the major selenium contributor in older samples with a peak concentration of ~50 ng/g (Table 2) at day 8. An unknown sulfur-selenium-containing compound with a retention time of 25 min (Figure 3) was present at higher concentrations in the month-old litter samples. Based on the late elution of the peak, this compound could be dimethyl selenodisulfide, CH<sub>3</sub>SeSSCH<sub>3</sub> (DMSSeS), which has a boiling point of ~192°C and was identified for the first time in headspace gases of bacterial cultures [2].

Table 2. Concentration of target selenium compounds in incubated broiler chicken litter samples.

Incubation period (day)	Dimethyl selenide (ng/g)	Dimethyl diselenide (ng/g)	Diethyl selenide (ng/g)
0 <sup>a</sup>	n.d.	n.d.	n.d.
2	2.225	1.11	0.165
8	46.55	3.04	0.75
30	16.52	0.26	1.23

<sup>a</sup> Duplicate samples were analyzed within 2 hours of preparation.

<sup>b</sup> Not detected

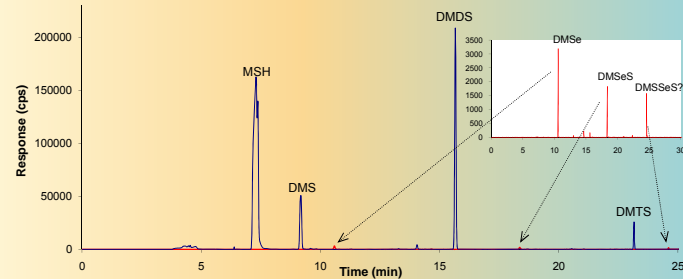


Figure 3. VD-GC-ICPMS chromatograms of a 30 days-old broiler chicken litter sample.

## 5. CONCLUSION / FUTURE WORK

The vacuum distillation/extraction and separation approach reported here is not unique to this study [1]. The use of ICP-MS as an element specific detector however, made it a novel yet powerful tool to measure volatile metal/metalloid-containing compounds at their low, environmentally relevant concentrations. The dual usage of VD-GC-ICP-MS and VD-GC-MS made it possible to positively identify volatile selenium, sulfur and sulfur-selenium compounds biogenerated in broiler chicken litter. Preliminary results of this study indicate that there is a great possibility that most of the selenium content of broiler litter could be gasified during incubation/fermentation to produce biofuels. Study on the determination of emission products in broiler chicken litter is still on-going.

## 6. ACKNOWLEDGEMENTS

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## REFERENCES

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