A41A-0075 56

Michigan Tech
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Quantification of Terpenes by 1DGC-MS and 2DGC-TOF-MS

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I. INTRODUCTION

On a global scale, biogenic emissions account for 90% of the reduced carbon emitted to the atmosphere (□1000±600Tg/y). Biogenic emissions of organic compounds mostly occur in the gas phase, however, partitioning between the gas and particle phase is also possible. The use of novel techniques, such as comprehensive gas chromatography (GC×GC) has demonstrated that a substantial fraction of organic species in the gas and particle-associated phases have not been identified and measured, and thus, are not considered in biogenic emission inventories.

Deciduous and coniferous forests are the principal emitters of a complex mixture of isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), and sesquiterpenes ($C_{15}H_{24}$). Sesquiterpenes are readily oxidized in the atmosphere producing secondary organic aerosols (SOA) with 100% yields. The SOA are hydrophilic and scatter light, and thus increase albedo and lead to a cooling effect. In addition, both monoterpene - and sesquiterpene-generated SOA are effective cloud condensation nuclei leading to an increase in the particle number concentration and to the formation of clouds that also increase albedo.

The objective of this study was to resolve and identify the complex mixture of terpenes in essential oils of plants by GC-MS. The motivation of this work was to develop analytical methodologies to investigate pathways of biogenic SOA formation.

II. METHODS

Seventeen terpene standards (8 monoterpenes, $C_{10}H_{16}$ (α-pinene, camphene, β-pinene, myrcene, 3-carene, limonene, ocimene and terpinolene), 1 monoterpene alcohol, $C_{10}H_{18}O$ (linalool), 5 sesquiterpenes $C_{15}H_{24}$ (copaene, α-cedrene, caryophylene, humulene, farnesene) and 3 sesquiterpene alcohols $C_{15}H_{26}O$ (cis-nerolidol, trans-nerolidol and cedrol)) were prepared and analyzed by gas chromatography-mass spectrometry (GC-MS). Retention times and mass spectra were obtained by 1DGC-MS and 2DGC-TOF-MS.

Essential oils recovered from leaves and needles of *Picea mariana* (Black Spruce), *Pinus sylvestris* (Scots Pine) and *Thuja occidentalis* (Cedar) by steam distillation were diluted to 10 µg/µl and injected into the 1DGC-MS instruments to study their composition.

TDS-1DGC-MS

Sample introduction: Thermal Desorption Unit (TDU).
Injection: Manual injection of 2 µL using a stainless steel minitube. Splitless injection.
Thermal desorption temperature: 200°C, 10 min hold.
Cool inlet system (CIS) temperature: 0°C

GC: Agilent 5890 Gas Chromatograph
Inlet: Split/Splitless
Carrier gas: H_2 at 1.8 ml/min
Column: DB5, 60 m × 0.25 mm
GC oven: 70°C (1 min hold) to 250°C (5 min hold) at 7°C/min.

MS detector: HP 5972
Ionization: EI at –70eV
Ion Source temperature: 200°C
Spectral acquisition rate: 2 spectra/sec
Acquired mass range: 50-425 u

Data analysis and library hits:
Chemstation vB.01.00, 1998. Wiley138 library

2DGC-TOF-MS

Sample introduction:
Injection port temperature: 200°C
Injection: Manual injection of 2 µL (splitless).

GC: Agilent 6890 Gas Chromatograph
Inlet: Split/Splitless
Carrier gas: He at 1.0 ml/min
Primary column: DB-5MS, 30 m × 0.25 mm × 0.25 µm
Secondary column: DB17, 10m × 0.10 mm × 0.10 µm
Primary oven: 70°C (1min hold) to 250°C (5 min hold) at 7°C/min.
Secondary oven: 5°C offset from primary oven
Modulator: 30°C offset from primary oven
Modulation time: 5s
Transfer line temperature: 250°C

MS detector: TOF-MS Pegasus 4D
Ionization: EI at –70eV
Ion Source temperature: 200°C
Spectral acquisition rate: 200 spectra/sec
Acquired mass range: 35-400 u
Acquisition delay: 80 s

Data analysis and library hits:
ChromaTOF v4.22. May 7, 2009. NIST library

III. RESULTS

Black Spruce

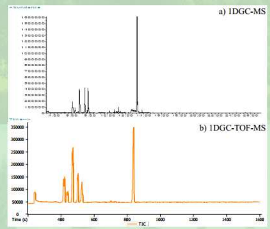

Figure 1. Total Ion Chromatogram (TIC) of Black Spruce by a) 1DGC-MS and b) GC-TOF-MS

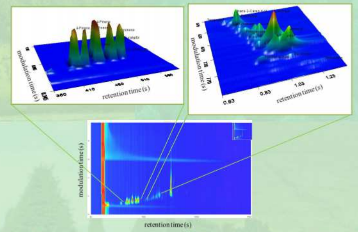

Figure 2. Total Ion Chromatogram (TIC) of Black Spruce by 2DGC-TOF-MS

Table 1. Comparison of terpenes identified by 2DGC-TOF-MS and 1DGC-MS in Black Spruce*.

Compound name	Molecular Weight	Formula	2DGC-TOF-MS R.T. (min)	2DGC-TOF-MS Similarity	2DGC-TOF-MS Area	1DGC-MS R.T. (min)	1DGC-MS Similarity	1DGC-MS Area
α-Pinene	136	C10H16	7.06	933	23173557	6.03	91	5911574
Camphene	136	C10H16	7.26	955	815397	6.32	97	2629048
Camphene	136	C10H16	7.38	956	933253	6.4	92	2139060
β-Pinene	136	C10H16	7.81	962	25680137	6.84	94	15887340
3-Carene	136	C10H16	8.41	924	133335	7.44	95	11368746
Limonene	136	C10H16	8.78	948	4455379	7.8	93	2437064
L-camphor	152	C10H16O	11.22	932	138986	10.3	68	236134
Borneol	154	C10H18O	11.71	909	967442	10.74	83	1479270

* In addition to the compounds presented in the table, 56 terpenes and 12 acetates were identified by 2DGC-TOF-MS

Scots Pine

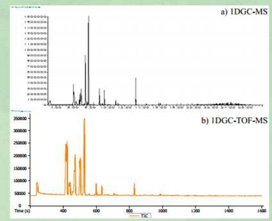

Figure 3. Total Ion Chromatogram (TIC) of Scots Pine by a) 1DGC-MS and b) 1DGC-TOF-MS

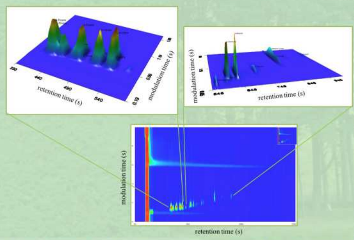

Figure 4. Total Ion Chromatogram (TIC) of Scots Pine by 2DGC-TOFMS

Table 2. Comparison of terpenes identified by 2DGC-TOF-MS and 1DGC-MS in Scots Pine*.

Compound name	Molecular Weight	Formula	2DGC-TOF-MS R.T. (min)	2DGC-TOF-MS Similarity	2DGC-TOF-MS Area	1DGC-MS R.T. (min)	1DGC-MS Similarity	1DGC-MS Area
α-Pinene	136	C10H16	7.06	934	2176588	6.13	95	7442705
Camphene	136	C10H16	7.25	958	902333	6.33	93	2633849
β-Pinene	136	C10H16	7.88	949	1056759	6.84	95	6405117
3-Carene	136	C10H16	8.41	920	203079	7.44	96	20461949
Limonene	136	C10H16	8.79	959	55481857	7.8	94	51471961
Gamma terpinene	136	C10H16	9.28	816	549180	8.39	91	993073
Fenchone	152	C10H16O	10.00	958	9429468	9.06	90	6812892
Thujone	152	C10H16O	10.54	892	2036806	9.65	70	5391105
Junipen	204	C15H24	16.39	918	134795	15.96	53	696762
Caryophyllene	204	C15H24	16.50	944	152742	16.16	76	823451
Humulene	204	C15H24	17.14	927	63979	16.82	64	216558
δ-Cadinene	204	C15H24	18.12	905	52984	18.04	93	446752

* In addition to the compounds presented in the table, 53 terpenes and 3 acetates were identified by 2DGC-TOF-MS.

Cedar

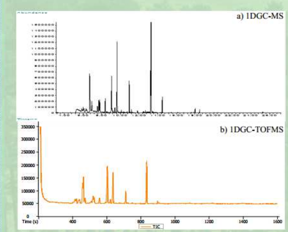

Figure 5. Total Ion Chromatogram (TIC) of Cedar by a) 1DGC-MS and b) 1DGC-TOFMS

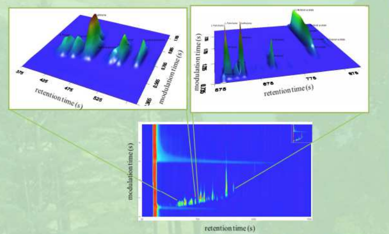

Figure 6. Total Ion Chromatogram (TIC) of Cedar by 2DGC-TOFMS

Table 3. Comparison of terpenes identified by 2DGC-TOF-MS and 1DGC-MS in Cedar*.

Compound name	Molecular Weight	Formula	2DGC-TOF-MS R.T. (min)	2DGC-TOF-MS Similarity	2DGC-TOF-MS Area	1DGC-MS R.T. (min)	1DGC-MS Similarity	1DGC-MS Area
α-Pinene	136	C10H16	7.04	928	3892097	6.03	87	3104719
δ-Camphene	136	C10H16	7.33	938	853836	6.39	90	3182255
Sabinene	136	C10H16	7.73	932	19146569	6.72	94	25021971
α-Myrcene	136	C10H16	7.89	910	1887520	6.95	80	9138426
Limonene	136	C10H16	8.77	931	925763	7.8	91	8867157
Gamma terpinene	136	C10H16	9.89	915	93871	8.39	94	6980541
L-Fenchone	152	C10H16O	10.07	956	45741123	9.06	90	15590627
Thujone	152	C10H16O	10.35	886	1219201	9.42	58	2644326
Isothujone	152	C10H16O	10.63	888	10683929	9.65	97	23986246
Camphor	152	C10H16O	11.23	913	161045	10.31	47	512052
L-terpinen-4-ol	154	C10H18O	11.86	889	4428734	10.98	96	10256285
α-Terpinyl acetate	196	C12H20O2	14.97	895	469046	14.51	91	4693670
α-Elemene	204	C15H24	15.83	874	18268	15.47	62	426371
Caryophyllene	204	C15H24	16.50	911	20247	16.15	58	372953
α-Muurolene	204	C15H24	17.79	683	37740	17.61	52	336229
Cadinene	204	C15H24	18.13	878	81419	18.02	93	1235634
Elemol	222	C15H26O	18.67	856	66721	18.5	58	1476121

* In addition to the compounds presented in the table, 41 terpenes and 9 acetates were identified by 2DGC-TOF-MS.

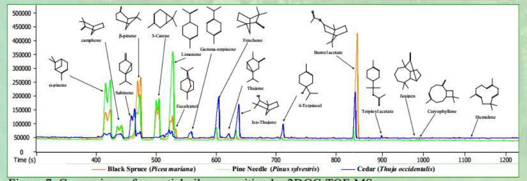

Figure 7. Comparison of essential oil composition by 2DGC-TOF-MS

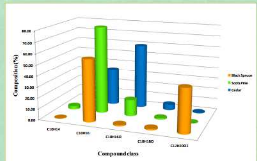

Figure 8*. Approximate composition of essential oils > 1% (assuming response factors are equal)

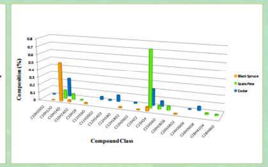

Figure 9*. Approximate composition of essential oils < 1% (assuming response factors are equal)

* Composition (%)= (total area of compound class/total area of all compounds)×100. The response factors of $C_{10}H_{16}$:$C_{15}H_{24}$ = 1:1.15 in standards. The response factors of $C_{10}H_{16}O$:$C_{15}H_{26}O$ = 1:0.55 in standards.

IV. Findings

1. Chromatography: Better resolution of terpene standards by 1DGC-MS compared to 1DGC-TOF-MS is attributed to the length of the column in the 1DGC-MS.

2. Identification of terpenes: Identification of the complex mixture of terpenes in essential oils was achieved by the combination of retention time analysis of authentic standards, deconvolution integration, 2DGC-TOFMS, and the Wiley and NIST libraries. The 2DGC-TOFMS allowed identification of 56 terpenes in Black Spruce, 53 in Scots Pine and 41 in Cedar, in comparison, 7, 12 and 17 terpenes, respectively, were identified by 1DGC-MS.

3. Essential oil composition: The composition of Black Spruce, Scots Pine and Cedar, was investigated. The monoterpenes ($C_{10}H_{16}$) compose 80% of Scots Pine, 57% of Black Spruce, and 34% of Cedar, whereas sesquiterpenes ($C_{15}H_{24}$) compose less than 1% of the studied tree species. Other than monoterpenes, the most abundant compounds were the following: Black Spruce was composed of 40% of $C_{12}H_{20}O_2$, Scots Pine was composed of 15% of $C_{10}H_{16}O$, and Cedar was composed of 60% of $C_{10}H_{16}O$. Possible alteration of the terpene distribution by steam distillation is unknown and requires further investigation.

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Acknowledgements

- The Mexican National Science Foundation, Consejo Nacional de Ciencia y Tecnología (CONACyT) for the fellowship to Rosa Flores.
- Dave Perram for technical support.