Analytical challenges in determination of Telomer 8-2 Alcohol and Telomer-derived fluorosurfactants and polymers in biological and environmental matrices.

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Why 8-2 Telomer B Alcohol?

Telomer alcohols: CF_3-$(CF_2)_n$-CH_2-CH_2-OH n=3,5,7,9,10, ...

8-2 Telomer B Alcohol: CF_3-$(CF_2)_7$-CH_2-CH_2-OH

Anionic Surfactants:

$(CF_3\text{-}(CF_2)_n\text{-}CH_2\text{-}CH_2\text{-}O)_x\text{-}PO(O^- NH_4^+)$

$CF_3\text{-}(CF_2)_n\text{-}CH_2\text{-}CH_2\text{-}S\text{-}\ CH_2\text{-}CH_2\text{-}COO^-\ Li^+$

$CF_3\text{-}(CF_2)_n\text{-}CH_2\text{-}CH_2\text{-}SO_3^-\ NH_4^+$

Non-ionic Surfactants:

$CF_3\text{-}(CF_2)_n\text{-}CH_2\text{-}CH_2\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_xH$

Polymers:

- urethane: MW ~3500
- acrylate: MW ~35,000

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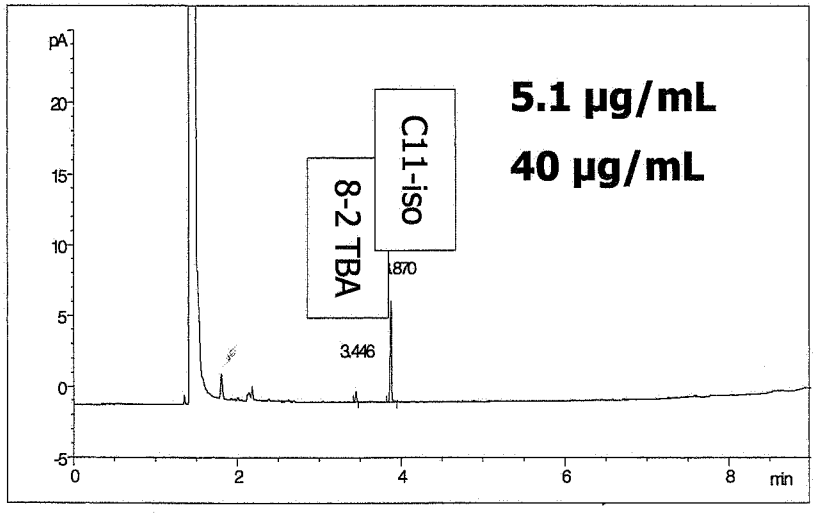
Analytical options for 8-2 Telomer B Alcohol

Properties:
- Structure: CF_3-$(CF_2)_7$-CH_2-CH_2-OH
- Water solubility: 150 µg/L
- Melting point: 44°C
- Boiling point: 213°C at 760 mm Hg
- Vapor pressure: 3 Pa at 21°C
- UV: none for 225-400 nm

1. GC-FID



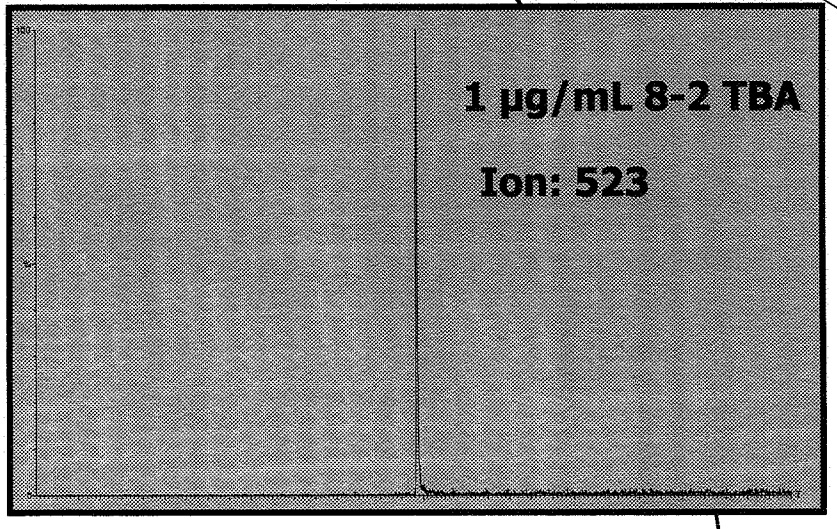
5.1 µg/mL

40 µg/mL

2. GC-MS:

- subject of this presentation

3. LC-MS



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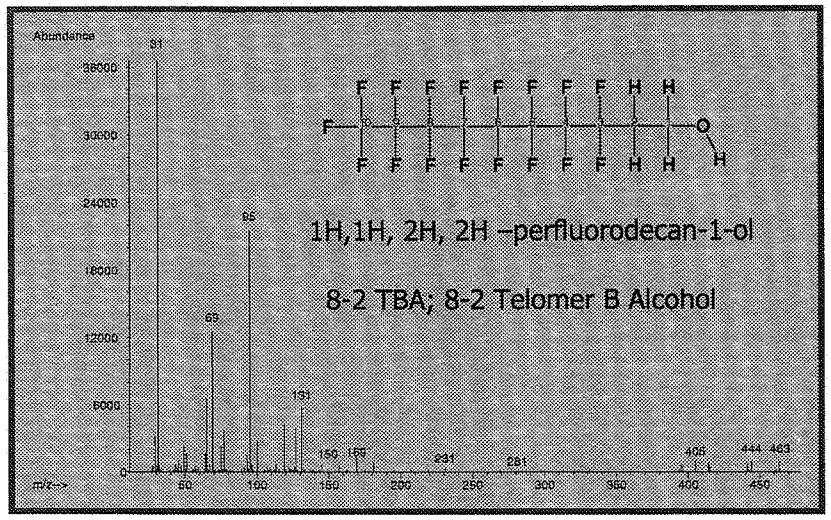
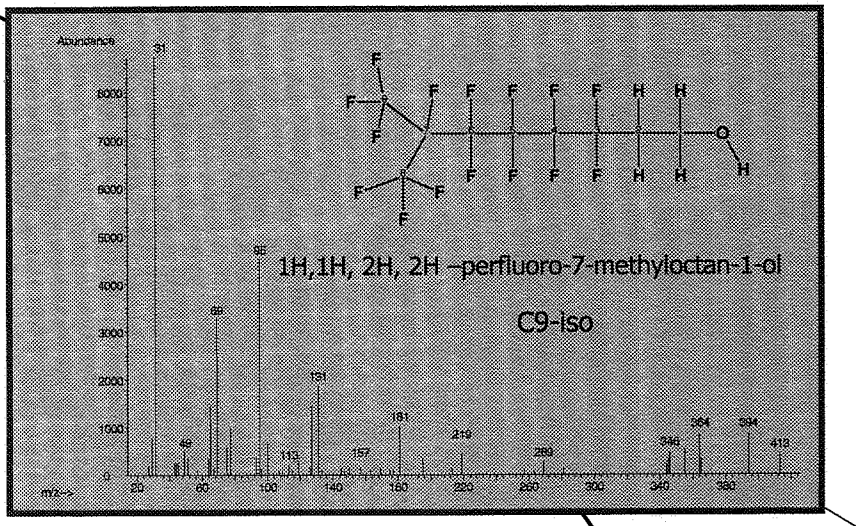
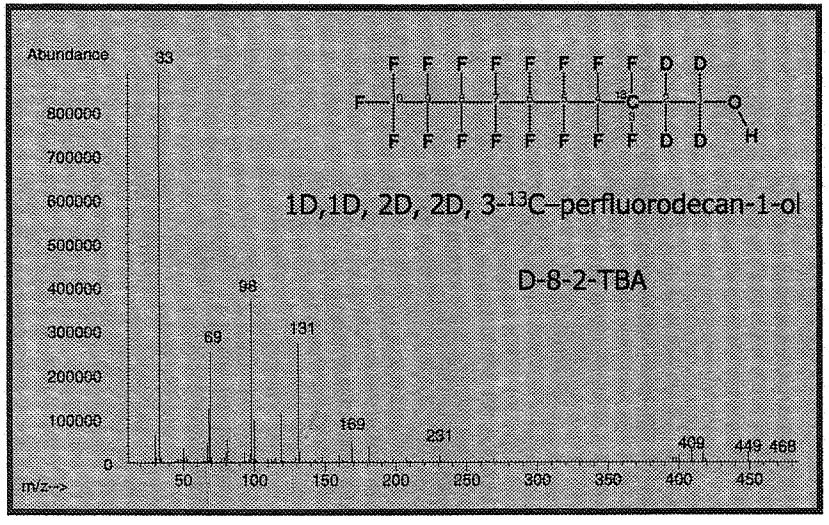
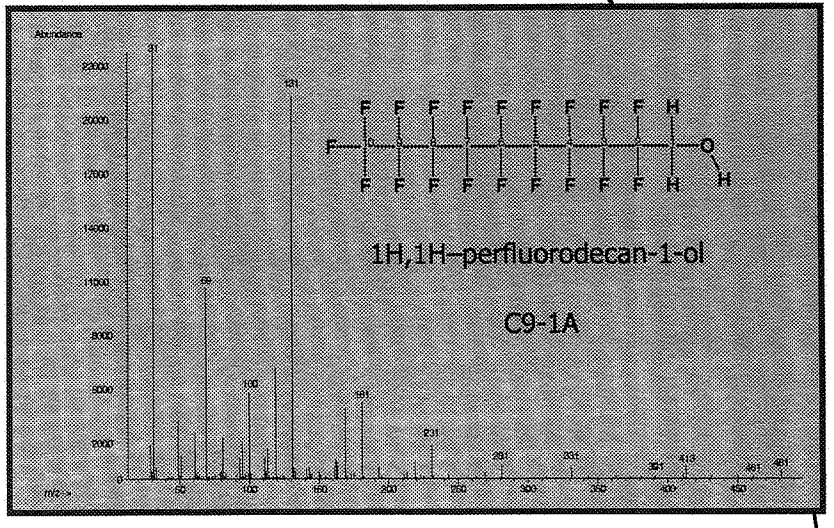
Basics of GC-MS method – EI spectra



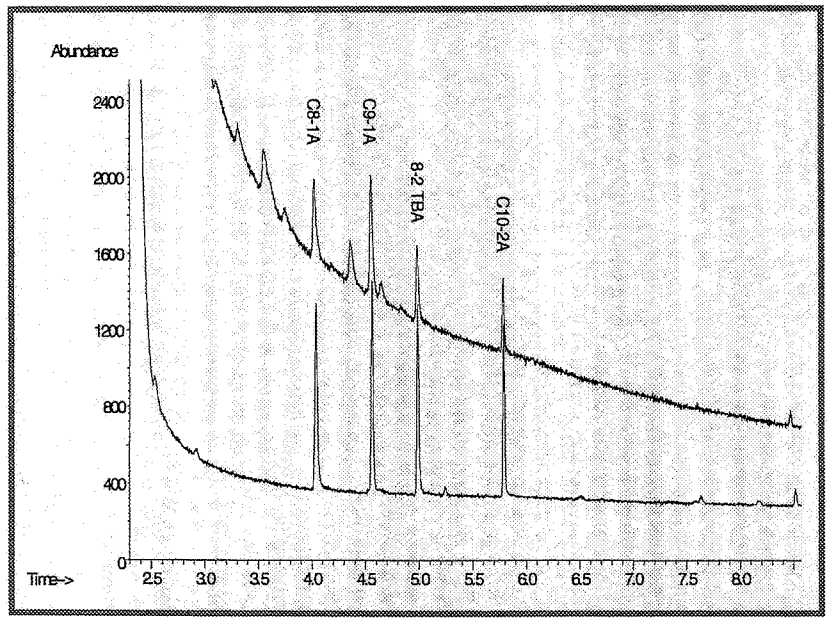






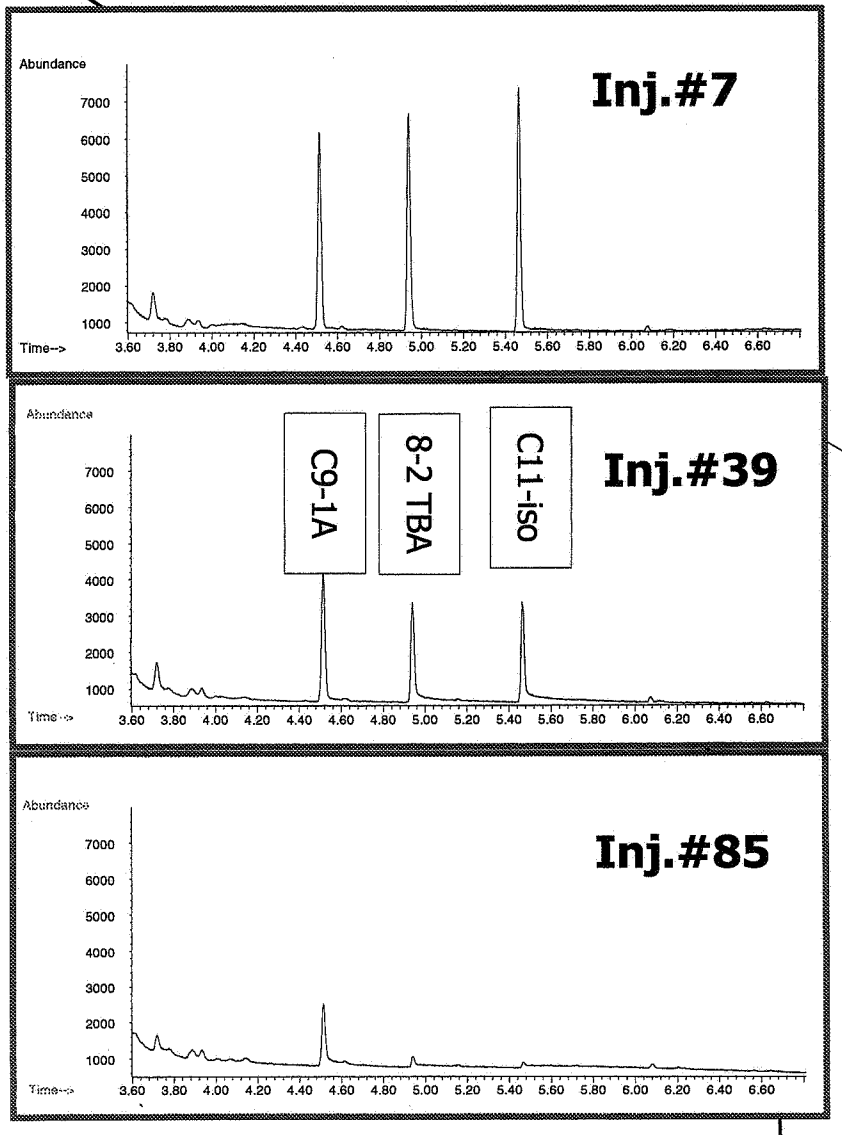
Basics of GC-MS method – Chromatography

Solvents



MTBE
Ethyl Acetate
MeOH
IPA

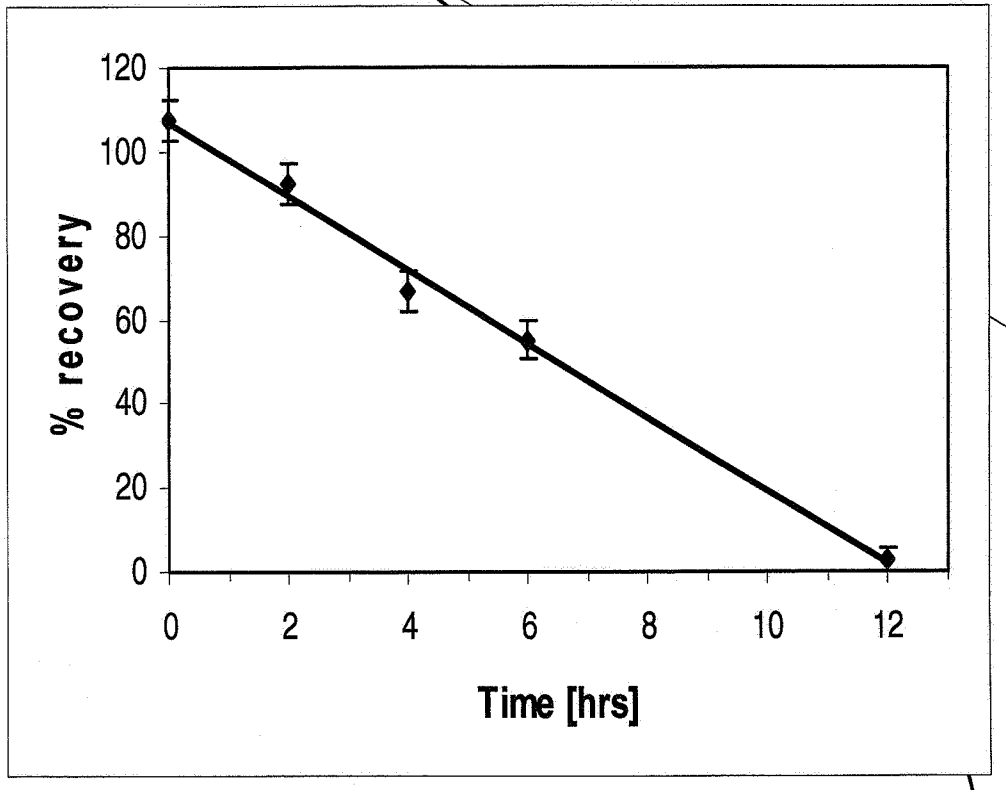
Column performance



8-2 TBA – headspace losses from water

Experiment

10 mL glass vial;
10 mL water;
8-2 TBA
*at **150 µg/L***



Environmental waters – method validation and sample storage

Experiment

10 mL glass vial;
5 mL water;
*8-2 TBA at **150** **µg/L***

Results (% recovery ± st. dev.)

Water type	1 hr RT	1 week Frozen	1 week RT	1 week RT (No foil)	1 month Frozen	1 month RT
Well	102±6	98±5	64±14	35±4	100±9	24±16
Pond	98±2	91±6	57±12	30±2	104±2	26±15
Creek	99±6	86±5	53±6	29±8	100±2	15±14
Sea	96±2	86±5	92±9	29±8	99±2	88±16

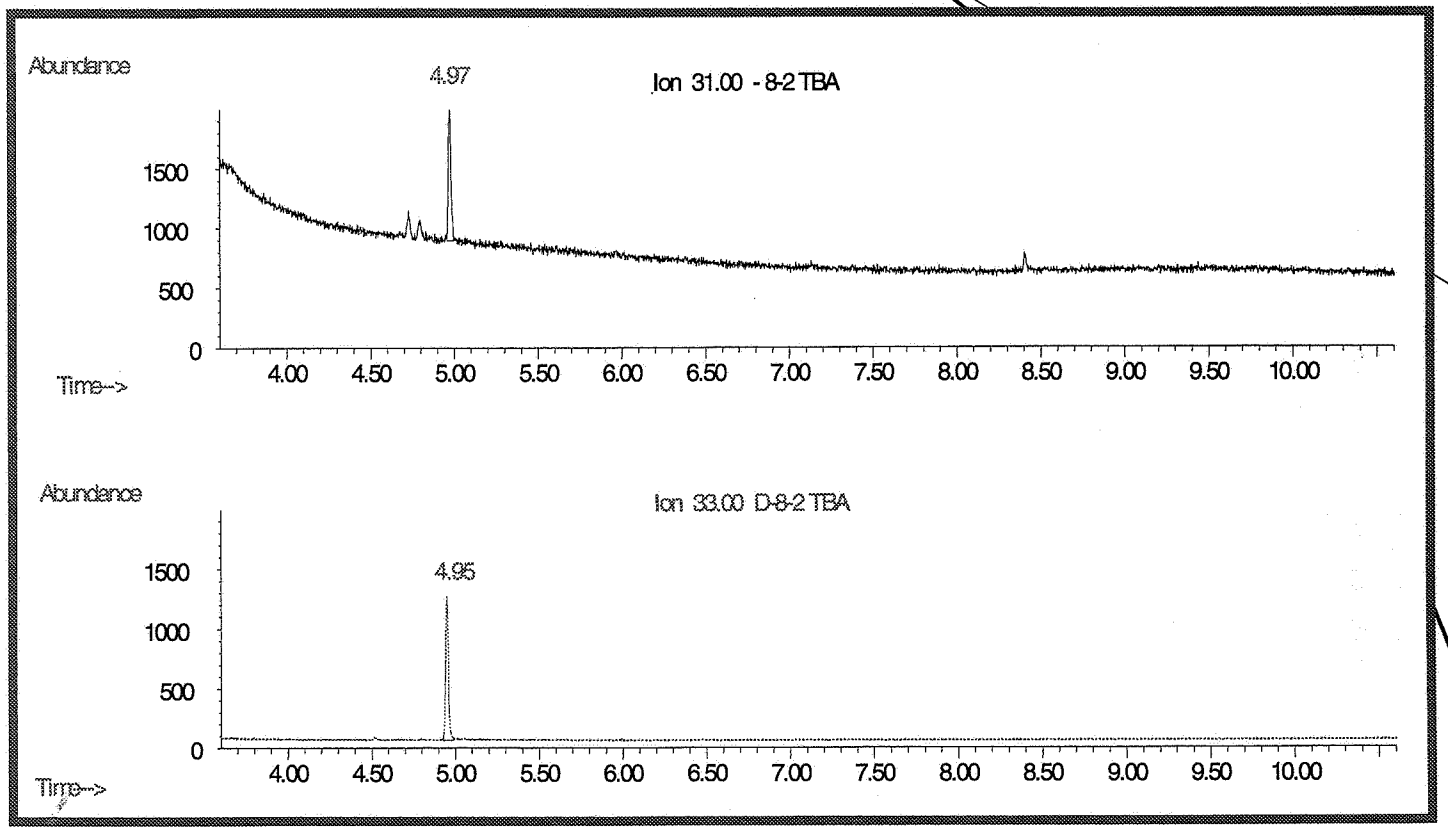
Environmental waters – validation and sample storage

Results (% recovery ± st. dev.)
15 µg/L 8-2 TBA

Water type	1 hr RT	1 week Frozen	1 week RT	1 week RT (no foil)
Well	94±5	108±4	28±4	14±4
Pond	94±6	----	----	----
Creek	91±6	----	----	----
Sea	94±5	----	----	----

Environmental waters – example chromatogram

15 µg/L 8-2 TBA in Sea water



8-2 TBA – soils

Procedure

Extraction:

2 g soil, spike 8-2 TBA; add 1 mL H_2O; extract with 6 mL hexane

Clean-up:

SPE: Si, 100 mg /10 mL (IST)

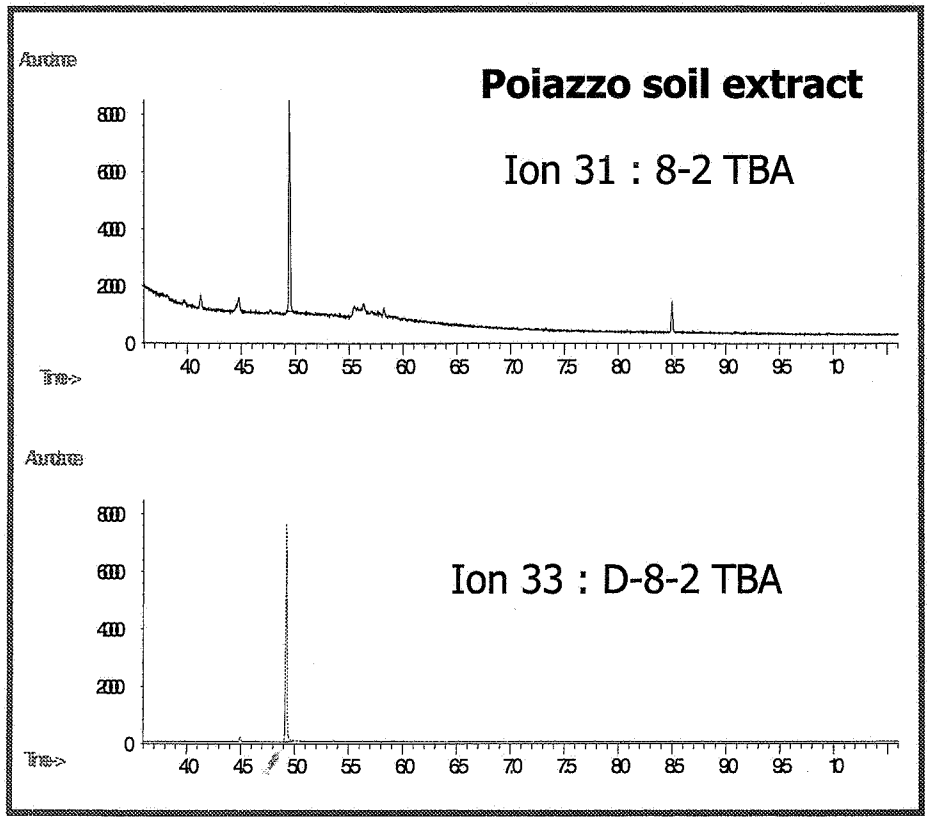
1. 2 mL IPA and 2 mL Hexane
2. Load hexane extract
3. Wash with 6 mL hexane
4. Elute with 1 mL IPA

Results for 150 µg/g spike

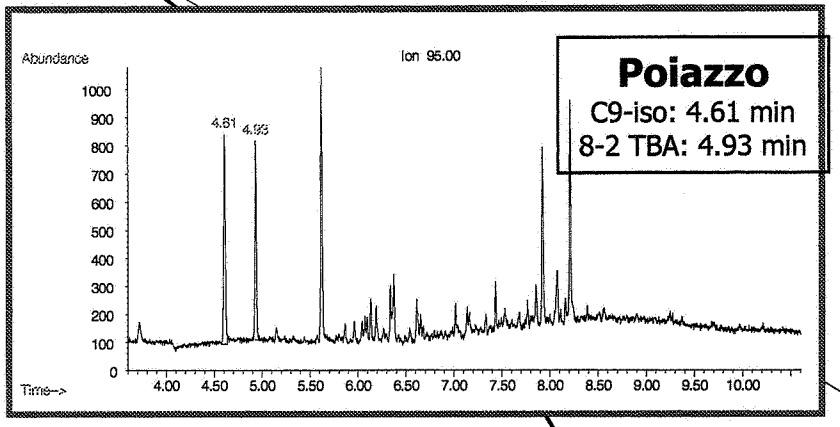
Soil type	Soil (% Rec. ±st.dev)	Soil extract (% Rec. ±st.dev)
Poiazzo (44% sand, 26% slit, 30% clay)	**87±4**	**98±1**
Key Port (17% sand, 62% slit, 21% clay)	**88±15**	**90±6**
Hildago (52% sand, 20% slit, 28% clay)	**81±11**	**92±7**
White Clay (98% sand, 2% slit)	**87±6**	**94±1**

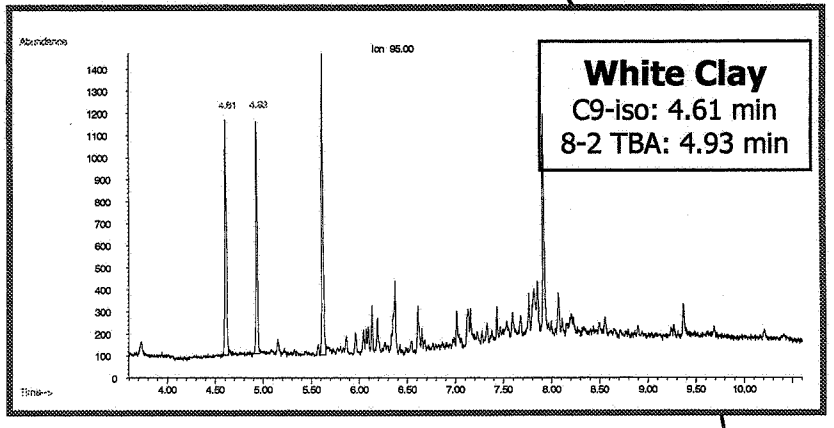
8-2 TBA – soil - chromatograms

Soil extracts



Soils





8-2 TBA – plasma and tissues procedures

Fat

Extraction:
0.3 g fat, (spike), dissolve in 6 mL heptane

Clean-up:

SPE: Si, 500 mg /10 mL (IST)

1. 1 mL acetone and 2 mL heptane
2. Load heptane extract
3. Wash with 6 mL heptane
4. Elute with 1 mL IPA

Liver
Kidney

Extraction:
0.5 g tissue; (spike), add 2 mL water, 15 µL $HClO_4$; extract with 6 mL hexane; 15 min vortex; centrifuge

Clean-up:

SPE: Si, 500 mg /10 mL (IST)

1. 1 mL IPA and 2 mL hexane
2. Load hexane extract
3. Wash with 6 mL hexane
4. Elute with 1 mL IPA

Plasma

Extraction:
0.25 mL plasma + 0.25 mL water +1 mL MTBE; 15 min vortex; centrifuge

No Clean-up for plasma

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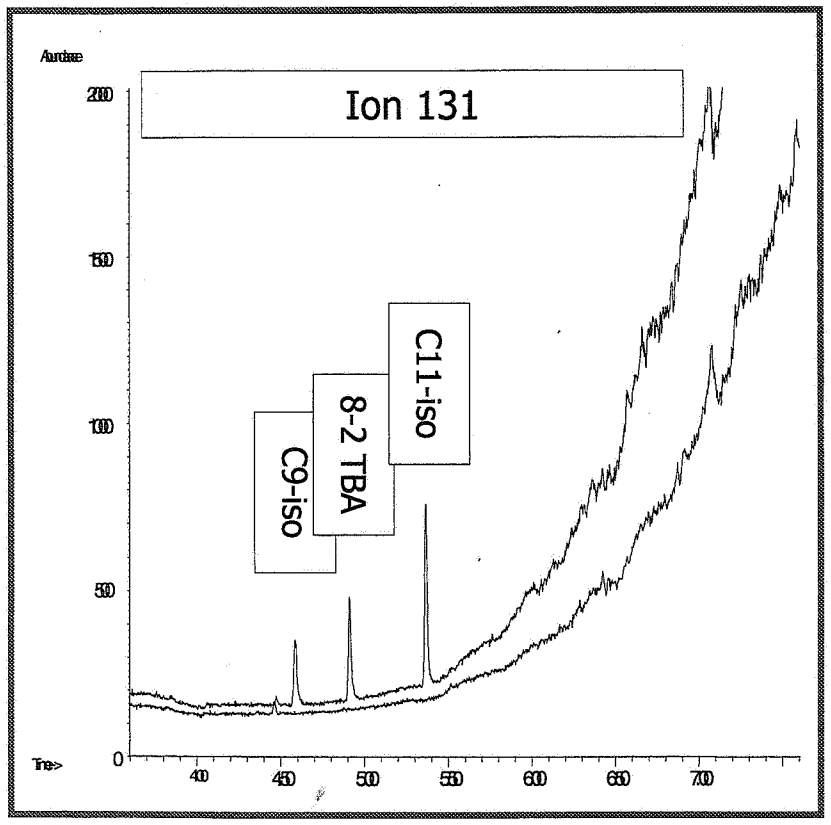
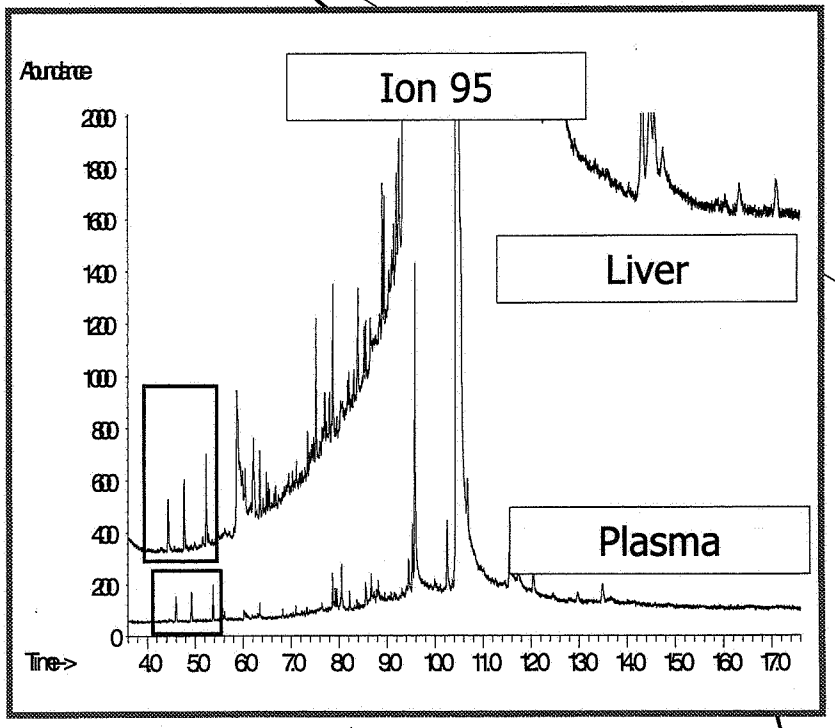
8-2 TBA – plasma and tissues chromatograms

Fat: 190 ng/g spike and blank



Plasma: 100 ng/mL spike
Liver: 200 ng/g spike



8-2 TBA – plasma and tissues results

Matrix	Spike Level	8-2 TBA (% Rec. ±st.dev)	C9-iso (% Rec. ±st.dev)	Estimated LOD
Fat	190 ng/g	63±1	67±10	12 ng/g
	950 ng/g	100±3	95±7	
Liver	100 ng/g	98±4	97±15	6.0 ng/g
	200 ng/g	80±5	79±9	
Kidney	100 ng/g	72±5	75±10	4.0 ng/g
Plasma	100 ng/mL	86±7	82±15	5.0 ng/mL
	200 ng/mL	113±11	104±17	

Summary

- 8-2 Telomer B alcohol is a challenging analyte because of its volatility and low water solubility;

  - low water solubility dictates the need for methods developed at LOQ;

  - extraction solvent choice is critical in achieving required sensitivity, precision, and GC/MS system performance;

  - volatility losses from water are rapid and significant;

  - solvent exchange is not an option, limiting the choices for sample concentration or/and clean-up;

  - samples should be stored frozen;

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Summary

- demonstrated the analytical procedures for analysis of 8-2 Telomer B alcohol in environmental waters, soils, rat plasma, and tissues;

  - extracts derived from complex matrices (soil, tissues) require clean-up;

  - maintaining column performance is critical for reliable quantitation and maintaining GC/MS sensitivity;

  - use of internal standards (especially isotopically labeled) is critical for accurate quantitation;

  - use of surrogates is important for accurate quantitation in biological matrices;

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