

Extended Abstract

The Analysis of Bayer Liquor by SPME-GC-MS of Derivatized Organic Poisons †

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The aim of this article was the gas chromatography–mass spectrometry (GC-MS) analysis of organic matter from a residual liquor sample (S.C. Alum S.A., Tulcea), extracted by the solid-phase microextraction method (SPMA) and derivatized with *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA) as the silylating agent. The trace organic matter from Bayer liquor (known as poisons) has the ability to inhibit $\text{Al}(\text{OH})_3$ (gibbsite) crystallization. The structure of the poisons is essential for understanding how inhibition is induced and consequently, how they can be removed [1,2]. The first step is the extraction of organic poisons from Bayer liquor by solid-phase microextraction (SPME) [3]. Due to the polar functionalized polyhydroxy compounds, and aliphatic and aromatic acids, the derivatization is required to produce more volatile compounds [4]. The most suitable technique of extracted and derivatized organic poisons from Bayer liquor has been shown to be GC-MS [1,5].

The experimental data for this paper were obtained on a gas chromatograph coupled with a mass spectrometer (GC-MS) produced by PerkinElmer, USA. A 50 mL aliquot of the residual liquor sample was acidified to precipitate $\text{Al}(\text{OH})_3$ which was removed by centrifugation. From the supernatant acidified with HCl at pH 2, a 20 mL aliquot was transferred to a test flask. The organic matter (poisons) in the sample vial was extracted by the SPME technique on a polyacrylate fiber (PA) of 85 μm . The polyacrylate fiber was immediately exposed in a heated ampoule (700 °C, 10 min), in nitrogen, to the derivatizing agent MTBSTFA/pyridine (7:3). This was followed by GC injection at 270 °C by desorption from the PA fiber for 5 min. The derivatized components of the residual liquor sample were separated chromatographically on a 60 m capillary column with stationary phase Elite-5 MS (phenyl-methyl silicone). The mass chromatogram (16–40 min) of the ions (m/z 73 + 75 + 147) with derivatized organic components is presented in Figure 1.

In Table 1, non-derivatized organic compounds with their molecular masses were obtained by subtracting the masses of the *tert*-butyldimethylsilyl (115-1) and trimethylsilyl (73-1) groups from the molecular masses of the compounds in Table 2.

The qualitative analysis of the derivatized organic components as *tert*-butyldimethylsilyl (TBDMS) or trimethylsilyl (TMS) derivatives (esters) of the residual liquor sample, separated by gas chromatography, was performed by comparing their mass spectra with the mass spectra in the NIST (the National Institute of Standards and Technology, U.S.) and NBS (the National Bureau of Standards, U.S.) mass spectrum libraries; 19 compounds were identified (Table 2). For example, see glycerin identification in Figure 2.

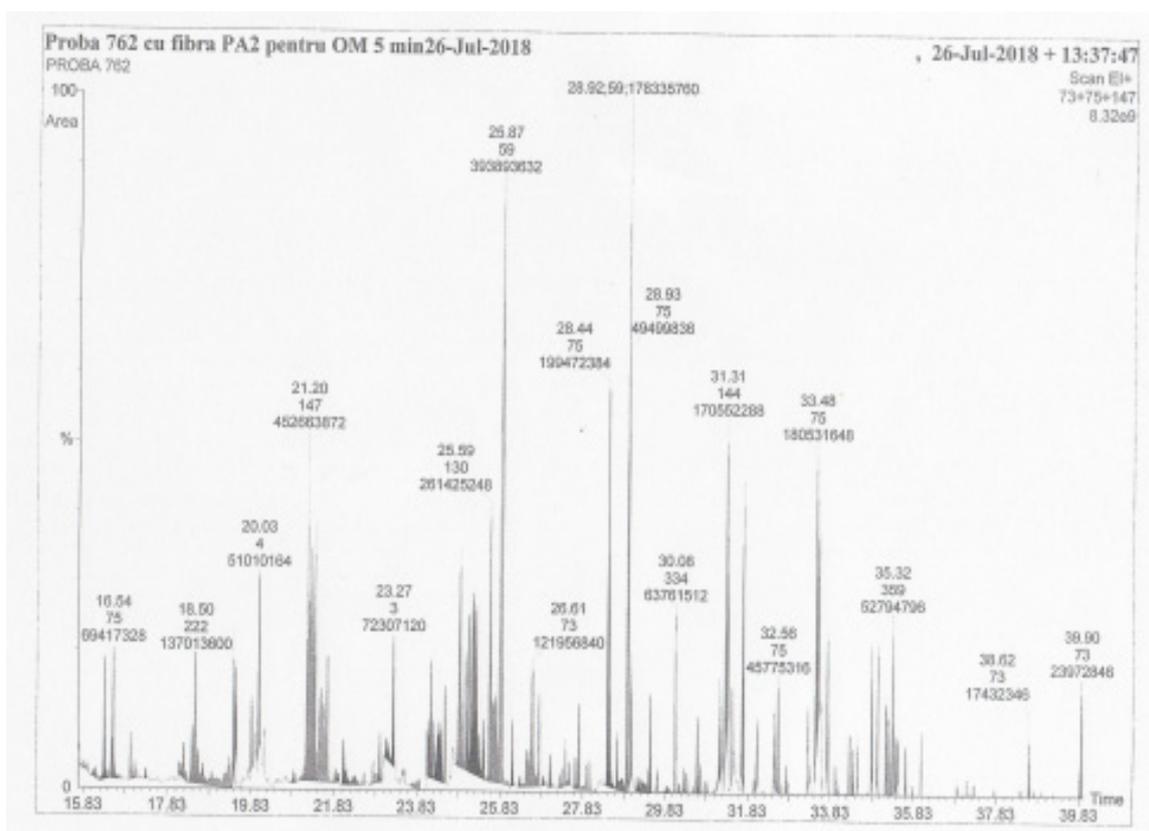


Figure 1. The mass chromatogram of organic compounds in the residual liquor sample.

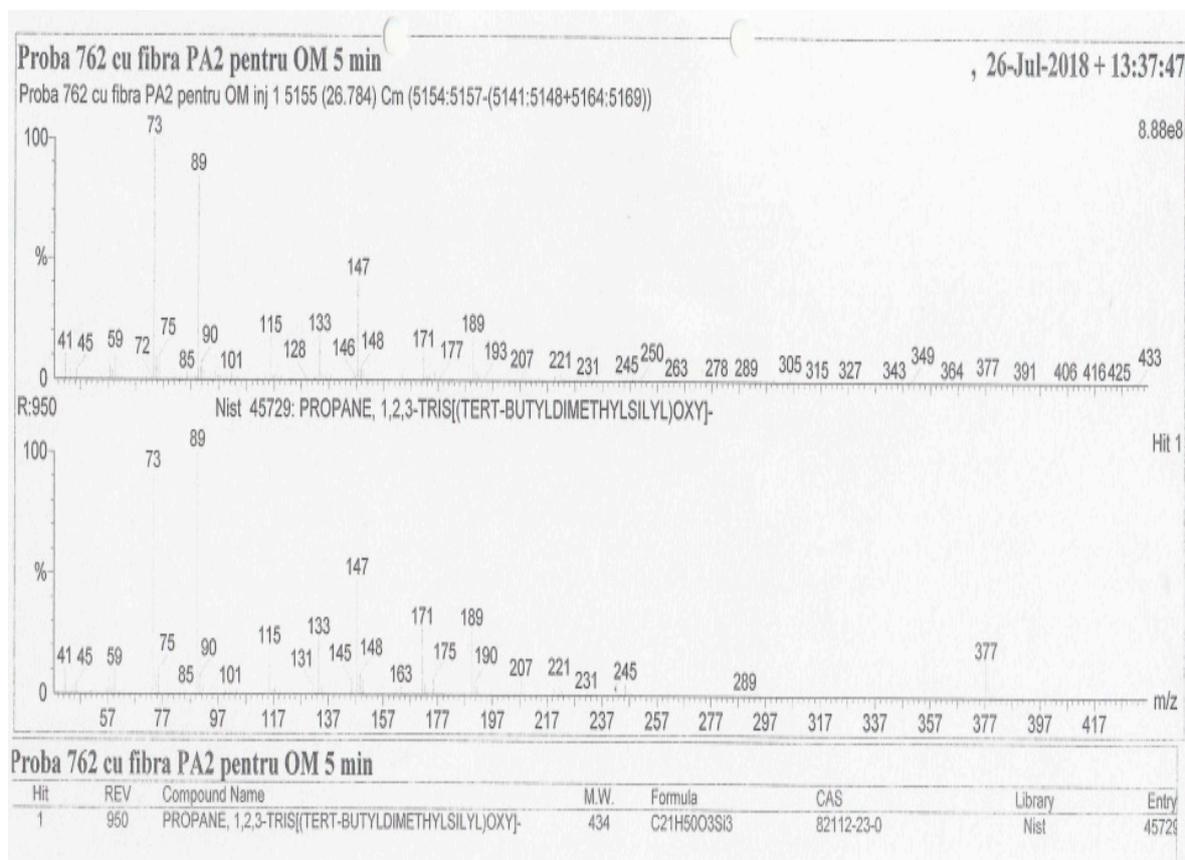


Figure 2. The identification of glycerin as *tert*-butyldimethylsilyl (TBDMS) ester (No. 10 in Table 2).

Table 1. The organic compounds from the residual liquor sample.

No.	Name of Components	M	Concentration, (mg/L)
1	Propanoic acid, 2-oxo-(pyruvic acid)	88	0.3
2	Butanoic acid, 3-methyl-(isovalerianic acid)	102	1.3
3	Pentanoic acid, 3-methyl-	116	0.1
4	Propandioic acid	104	2.7
5	Propanoic acid, 2-hydroxy	90	3.1
6	Benzoic acid	122	1.9
7	Carboxylic acid, <i>trans</i> -3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane	208	0.7
8	Tryptophan	204	1.1
9	Succinic acid	118	0.5
10	Propantriol (glycerin)	92	0.8
11	Acetic acid, 2-hydroxy-2,2-diphenyl-(benzyl acid)	228	0.9
12	5-Nonanol (dibutyl carbinol)	144	0.1
13	2-Methylcyclohexanol	114	0.9
14	Octadecanoic acid	284	1.4
15	9,12-Octadecadienoic acid	280	0.3
16	Pimaric acid	302	1.1
17	Isopimeric acid	302	0.6
18	Linolenic acid	302	1.0
19	Cyclopropanecarboxylic acid, 3-(2,2-dichlorovinyl)-2,2-dimethyl-, (3-phenoxyphenyl)methyl ester	390	0.3

Legend: M-molecular weight.

Table 2. The derivatized organic compounds from the residual liquor sample.

No.	Name of Components	M	TR (min.)	P (%)
1	Propanoic acid, 2-oxo-, trimethylsilyl ester	160	16.50	82.7
2	Butanoic acid, 3-methyl-tert-butyl dimethylsilyl ester	216	16.54	91.2
3	Pentanoic acid, 3-methyl-tert-butyl dimethylsilyl ester	230	18.13	90.3
4	Propandioic acid, bis (trimethylsilyl) ester	248	19.51	89.5
5	Propanoic acid, 2-[(<i>tert</i> -butyl dimethylsilyl)oxy]- <i>tert</i> -butyl dimethylsilyl ester	318	21.37	93.3
6	Benzoic acid, <i>tert</i> -butyl dimethylsilyl ester	236	21.50	91.4
7	Carboxylic acid, <i>trans</i> -3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane	322	24.50	90.4
8	<i>N,N',O</i> -tris (trimethylsilyl) tryptophan	420	25.00	86.2
9	Bis (<i>tert</i> -butyl dimethylsilyl) succinate	346	25.33	85.9
10	Propane, 1,2,3-tris[<i>tert</i> -butyl dimethylsilyl)oxy]-	434	26.78	95.0
11	Acetic acid, 2-hydroxy-2,2-diphenyl- <i>tert</i> -butyl dimethylsilyl ester	342	29.48	85.0
12	5-Nonanol-trimethylsilyl ester	216	30.88	87.5
13	Silanes, trimeth[(2-methylcyclohexyl)oxy]-, <i>cis</i> -	186	31.45	87.6
14	Octadecanoic acid, <i>tert</i> -butyl dimethylsilyl ester	398	33.76	83.8
15	9,12-Octadecadienoic- <i>tert</i> -butyl dimethylsilyl ester	394	34.38	85.9
16	Pimaric acid, trimethylsilyl ester	374	34.84	80.8
17	Isopimeric acid, trimethylsilyl ester	374	34.97	82.4
18	Linolenic acid, trimethylsilyl ester	350	35.17	82.2
19	Cyclopropanecarboxylic acid, 3-(2,2-dichlorovinyl)-2,2-dimethyl-, (3-phenoxyphenyl)methyl ester	390	36.10	95.0

Legend: M- Molecular weight; TR-GC retention time (min); P(%)-Probability (%) of matching the spectra in the sample with those in the NBS and NIST spectrum libraries.

Conclusions

The 19 organic compounds were identified in a residual liquor sample by comparing their mass spectra with the mass spectra in the NIST and NBS mass spectrum libraries.

The calculation of the concentration of the 19 identified components was performed from the area of their peaks in the mass chromatogram of the ions with m/z 73 + 75 + 147 and from the TOC analysis (854 mg/L) for the residual liquor sample.

The concentrations (in mg/L) of the 19 components identified in the residual liquor sample are given in Table 1.

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