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Direct Thermal Analysis of Solids - A Fast Method for the Determination of Halogenated Phenols and Anisols in Cork

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Abstract

Off-flavours in solid samples often cause analytical problems due to the necessity of sample pretreatment steps such as time consuming extractions followed by reconcentration of the resulting extracts and the danger of producing artifacts related to these methods.

In this paper the potential of a direct thermal desorption of the solid sample in combination with an intermediate cryo-focusing step in the insert-liner of a cooled injection system (CIS) followed by temperature programmed sample transfer to the analytical column, is discussed and demonstrated.

It will be shown that a reliable and fast method for the analysis of halogenated compounds in solid materials can be established without any sample pretreatment.

Introduction

Halogenated Phenols and Anisols, as 2,4,6-Trichlorophenol and -anisole, and also their bromo homologues, are well known for causing off- flavours in wine, beer and pharmaceuticals. These substances derive from pesticides as Pentachlorophenol, Lindane and Hexachlorobenzene, and also from 2,4,6-Tribromophenol. The Anisols are from microbiological origin by dehalogenation [1,2] and biomethylation [3]. The odour threshold of these substances is in the ppt range and so far can only be analysed after extraction and concentration of the tainted samples [4,5,6].

The analytical method newly demonstrated here uses direct thermal desorption to free the substances from their matrix without any other sample pretreatment. After cryo-focusing in the cooled injection system (CIS) the sample is analysed by GC-MS.

The analytical results obtained now allow to investigate, with samples as low as 3 mg, whether the fault of corkiness, i.e. 2,4,6-Trichloroanisole in wine corkstoppers, originates from the corkwoods as impurities or are produced during corkwood processing.

An off-flavour found in pharmaceuticals was analysed as 2,4,6-Tribromoanisole. It’s origin could be traced back to the polyethylene stoppers used for closing the bottles. These took up 2,4,6-Tribromoanisole derived from the Phenol by biomethylation. The Phenol was used for protection of the storing palettes against fire hazard and the infection by moulds.

EXPERIMENTAL

Instrumentation. The system consists of a thermodesorption system (TDS 2, Gerstel GmbH, Mülheim an der Ruhr, Germany, **Figure 1**), a temperature programmable cooled injection system (CIS 3, Gerstel GmbH, Mülheim an der Ruhr, Germany), a gas chromatograph (HP 5890 series II, Hewlett-Packard, Waldbronn, Germany) and a mass selective detector (HP 5972, Hewlett-Packard, Waldbronn, Germany).

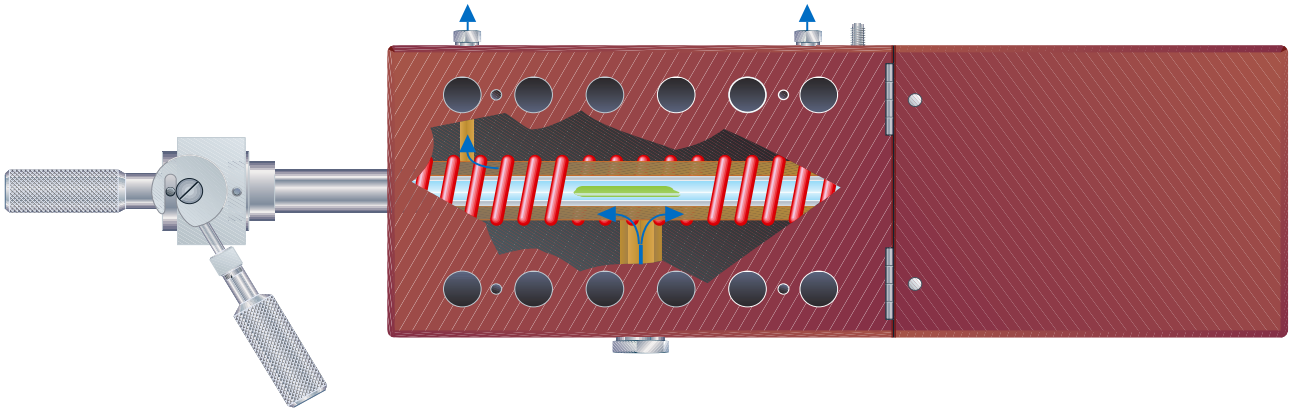

Figure 1. *Thermodesorption system TDS 2 (topview).*

Operation. A blank glass tube is filled with the sample and then inserted into the TDS 2 desorption chamber which is cooled down to subambient temperatures in order to prevent premature desorption. After purging the air out of the system, the tube is then heated to the desired temperature, while the carrier gas flowing through the tube transferres the volatiles in split- or splitless-mode (**Figure 2** and **3**) into the pre-cooled CIS, where they are cryofocused and concentrated.

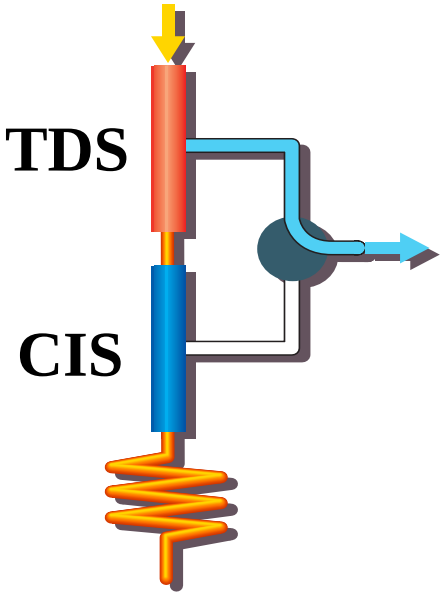

Figure 2. *Desorption principle, TDS in split-mode.*

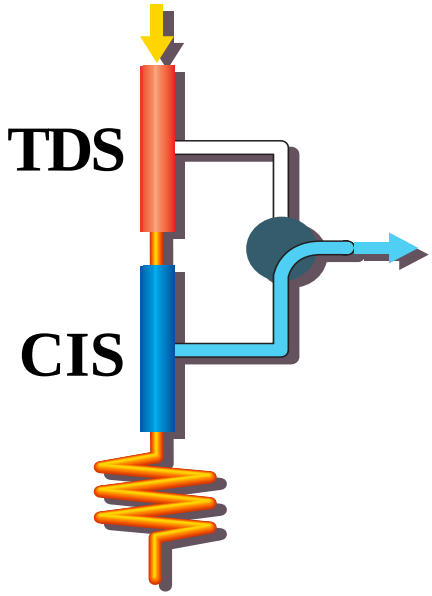

Figure 3. *Desorption principle, TDS in splitless-mode.*

After the desorption has finished the CIS is heated to the desired temperature to allow split or splitless transfer of the trapped compounds to the analytical column and further mass spectrometric detection. **Figure 4** describes the operation principle.

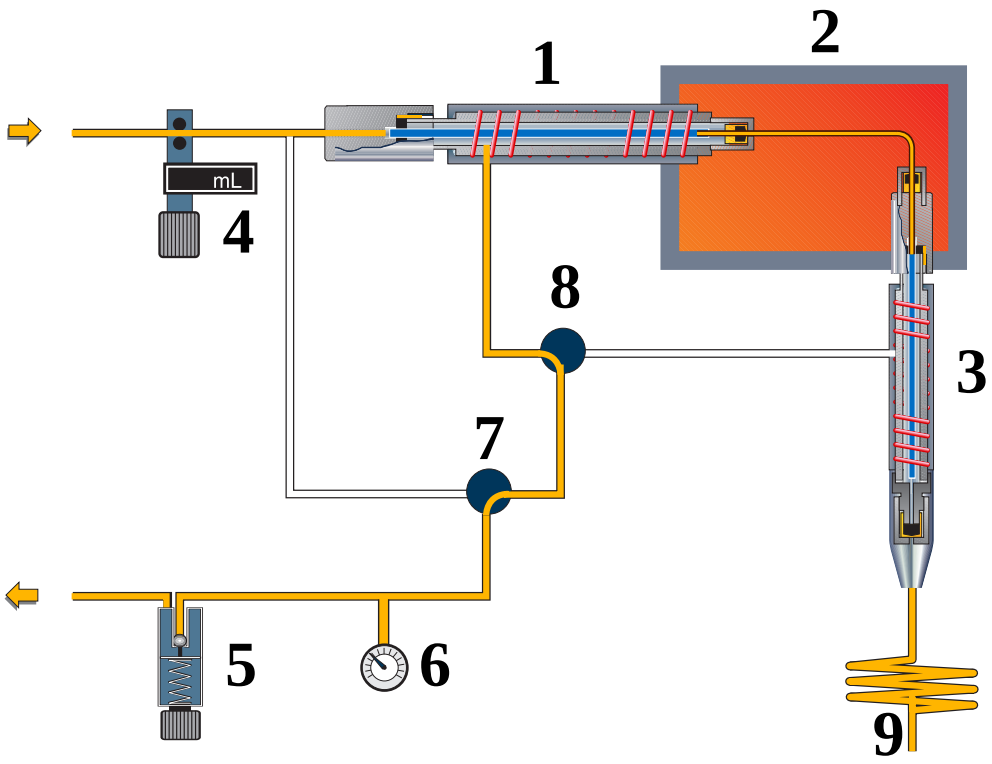

Figure 4. *Schematic of the applied system which consists of a thermodesorption system (1), a temperature controlled transfer capillary (2), a cooled injection system (3), standard backpressure Pneumatics with mass-flow controller (4), backpressure regulator (5), pressure gauge (6) and split/ splitless valve (7), including an additional 3/2-way solenoid (8) to switch the splitflow between TDS and CIS. The analytical column (9) is directly connected to a mass selective detector.*

Analysis conditions.

Column:	30 m HT 5 (SGE)	d_i = 0,22 mm		d_f = 0,1 µm
Pneumatics:	Carriergas	He	p_i = 100 kPa	split x:30
Temperatures:	TDS	60°C;	↗ 200°C;	20°C/min
	CIS	10°C;	↗ 300°C;	12°C/s
	Oven	60°C;	↗ 150°C;	10°C/min;
			↗ 380°C;	25°C/min
	MSD	280°C		

Sample Preparation. The only sample preparation to be done is grinding the material to be analysed to a size of less then 3 mm in diameter.

Results and Discussion

Figure 5 shows the chromatogram obtained when using 50 mg of cork material with a split ratio of 1:30 and a full scan mass range from 50 to 450 amu. On a 30 m HT-5 column with 0.22 mm internal diameter and a coating of 0.1 µm, two peaks are eluted between 8.00 and 8.30 minutes. The resulting mass spectra are clean enough for the identification of the 2,4,6-Trichloroanisole eluting at 8.16 min (scan 285) with a match quality 98% (**Figure 6**) and of 2,4,6-Trichlorophenol eluting at 8.33 min (scan 300) with a match quality of 87% (**Figure 7**).

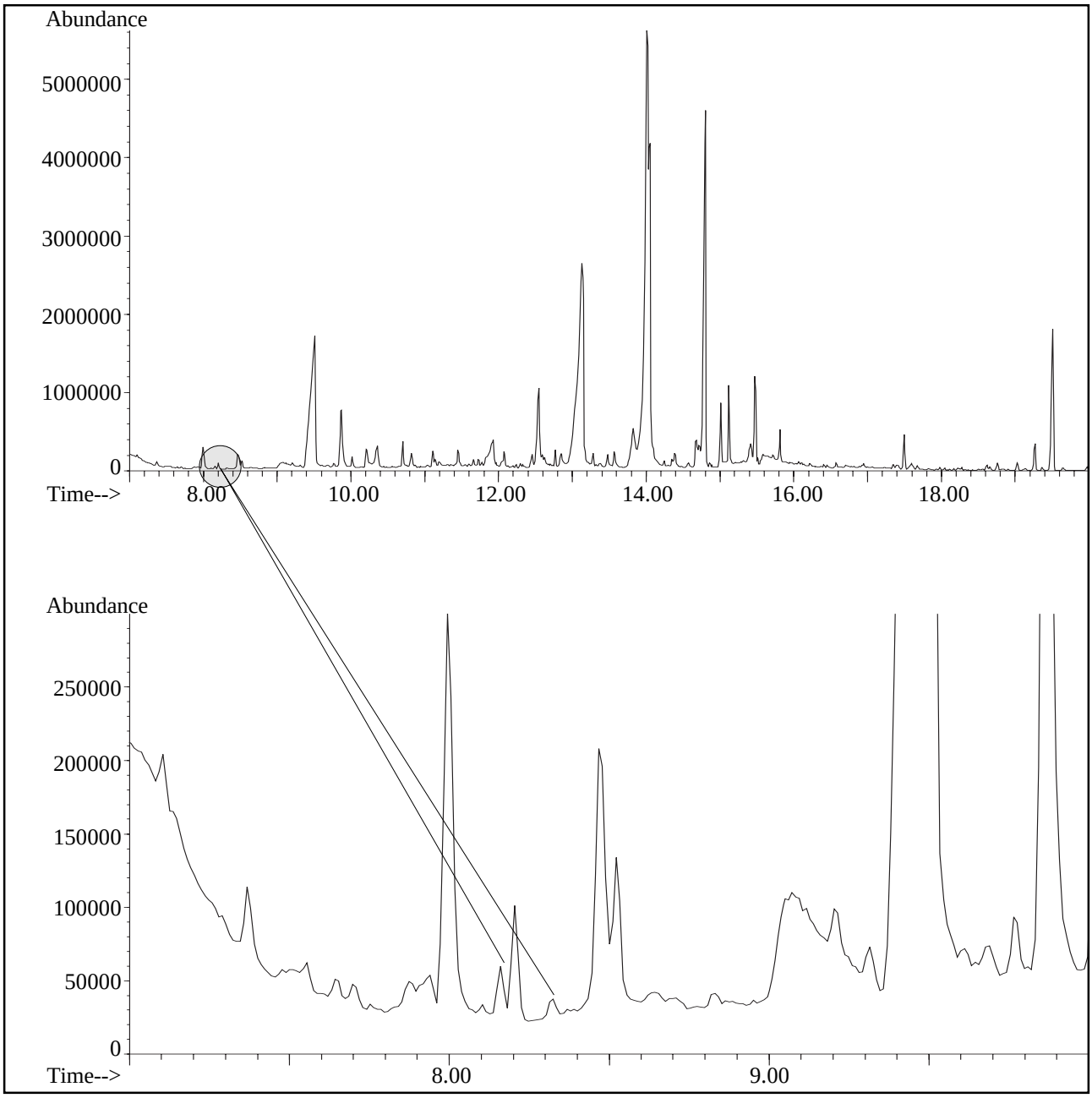

Figure 5. *Total ion chromatogram of cork, 50-450 amu, split 1:30.*

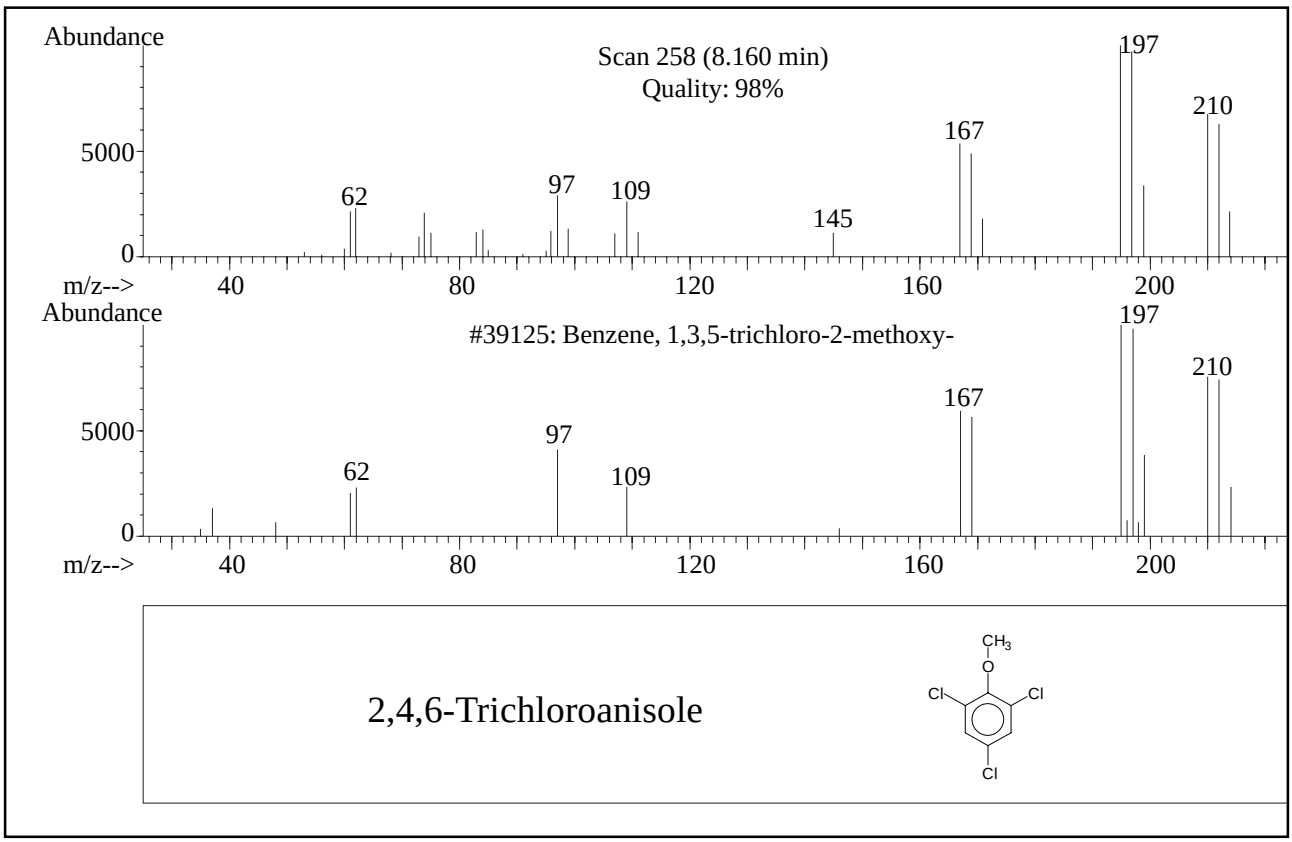

Figure 6. *Library search result for scan 28*5.

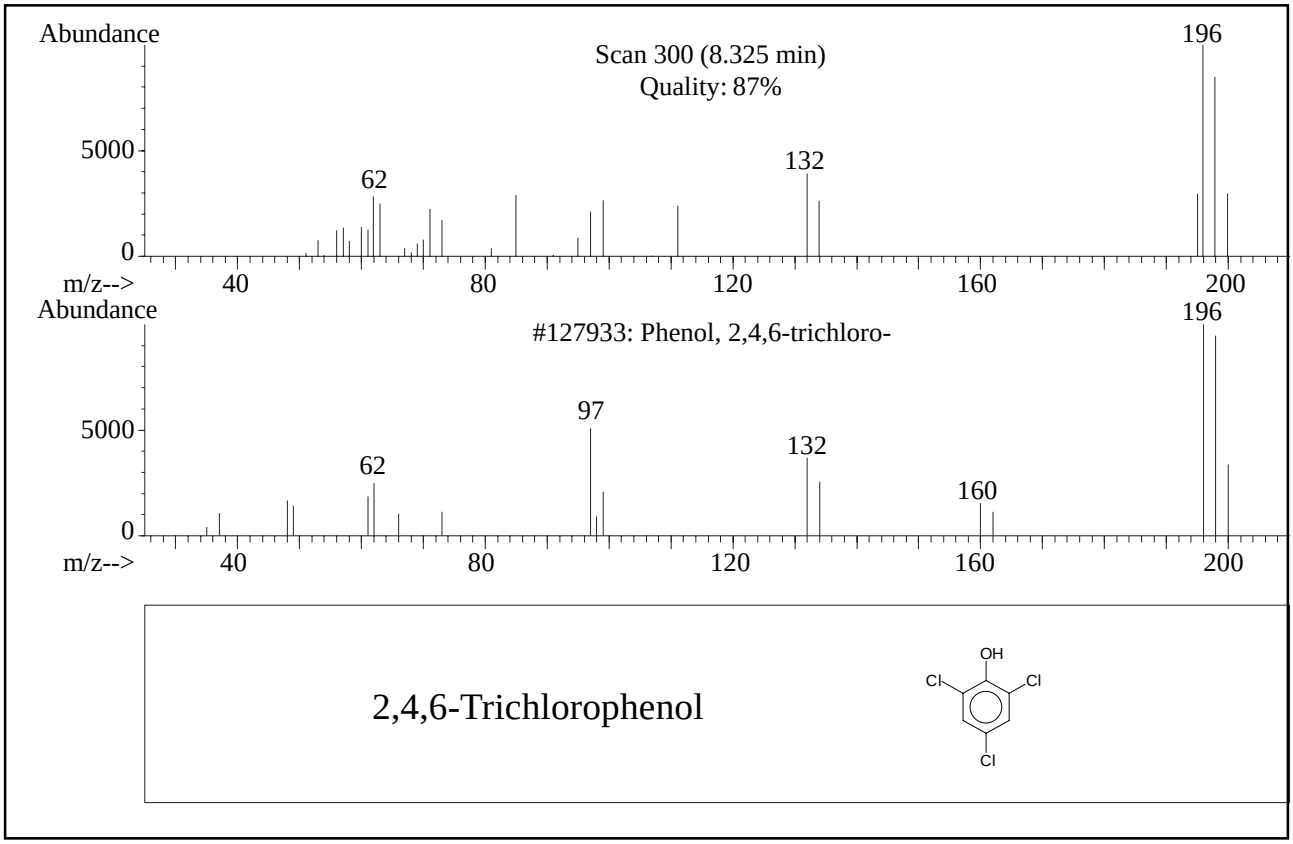

Figure 7. *Library search result for scan 300.*

In **Figure 8** and **10** these peaks are shown with the SIM- Ions 195, 197 and 210 for 2,4,6-Trichlorophenol with the relatively high abundance of 2500 and 196, 198 and 200 for the related Anisole, with an also relatively high abundance of nearly 5000, indicating the presence of these substances in the analysed sample. The sensitivity of this method is shown in **Figure 9** and **11**, where the abundances for both substances are only 100 for the Anisole and 400 for the Phenol.

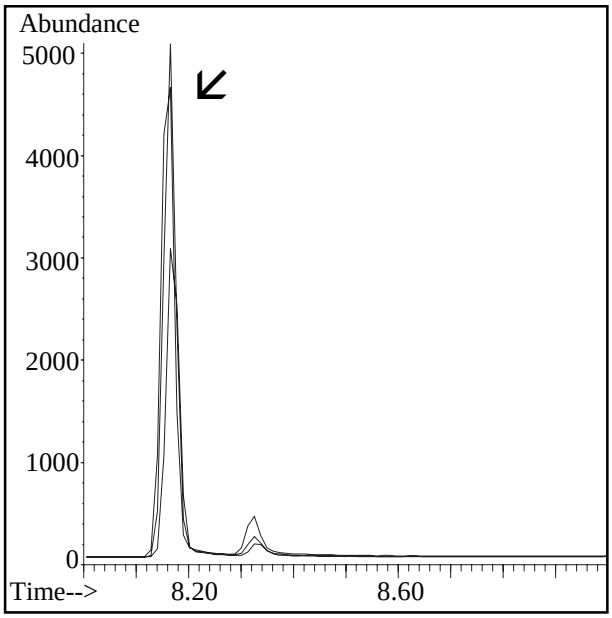

Figure 8. *SIM-trace of 2,4,6-Trichloroanisole, Ions 195/197/210, highest concentration found.*

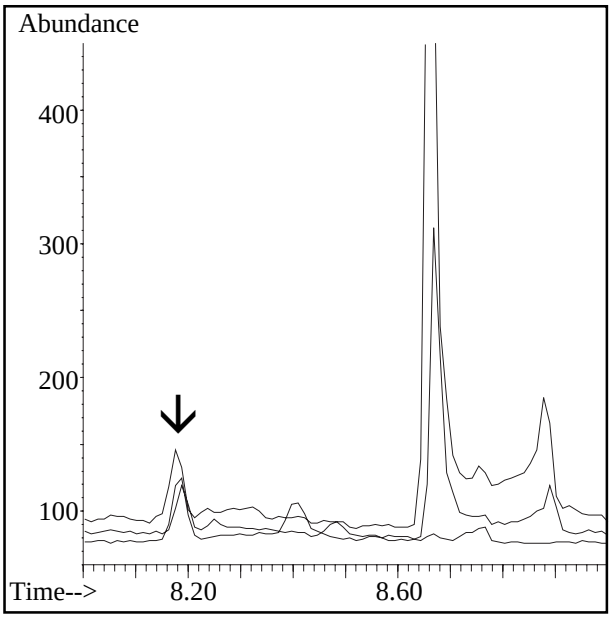

Figure 9. *SIM-trace of 2,4,6-Trichloroanisole, Ions 195/197/210, lowest concentration found.*

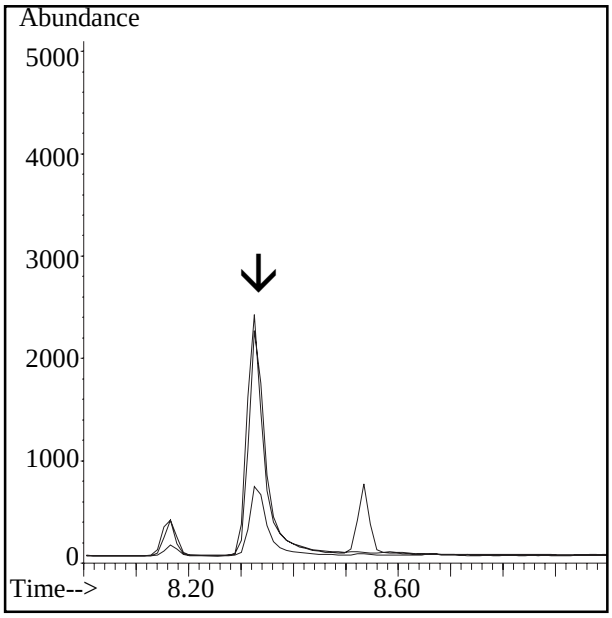

Figure 10. *Corresponding SIM-trace of 2,4,6-Trichlorophenol, Ions 196/198/200.*

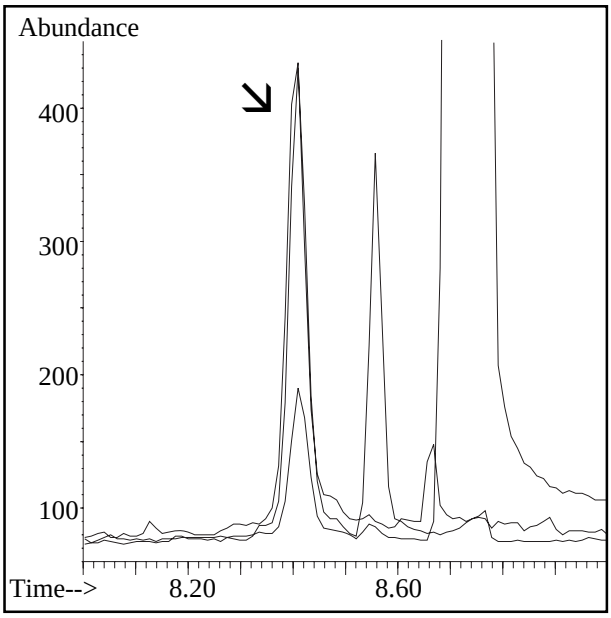

Figure 11. *Corresponding SIM-trace of 2,4,6-Trichlorophenol, Ions 196/198/200.*

This method can also either be used in the splitless mode or with higher amounts of material, when the expected concentrations of the tainting substance is too low.

The analysis of the tainted polyethylene were carried out with 200 mg of sample in splitless mode, with a full scan range of 50 to 550 amu with the same analytical column. **Figure 12** shows the resulting total ion chromatogram with a very small peak eluting between 12.00 and 12.30 minutes. This peak could be identified as 2,4,6-Tribromoanisole. The spectrum obtained had with 99% the highest possible match quality (**Figure 13**).
Under conditions with much lower concentrations of tainting material expected also selected ion monitoring can be used to further increase the sensitivity of the system.

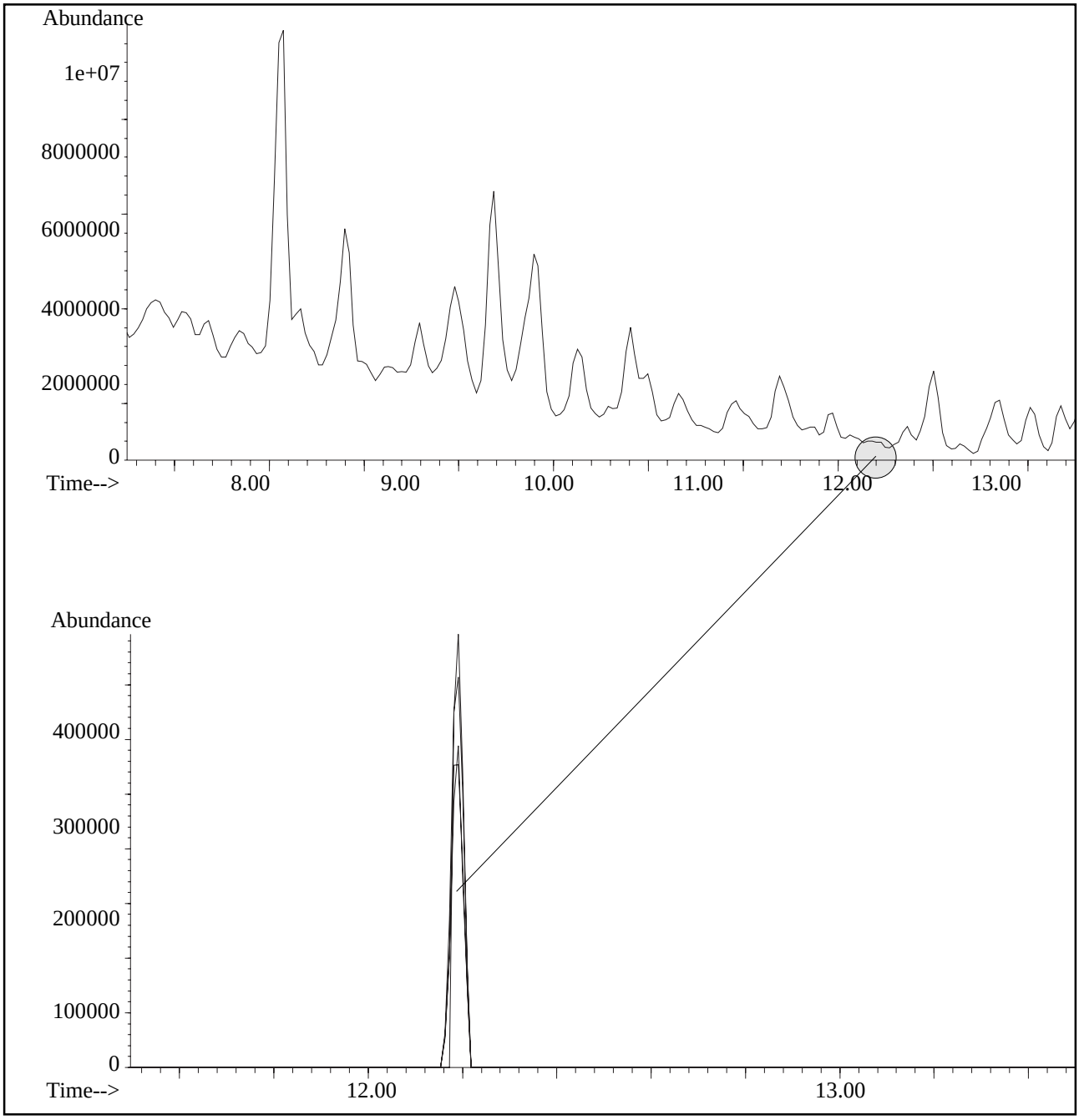

Figure 12. *Total ion chromatogram of polyethylene, scan 50-550 amu, splitless.*

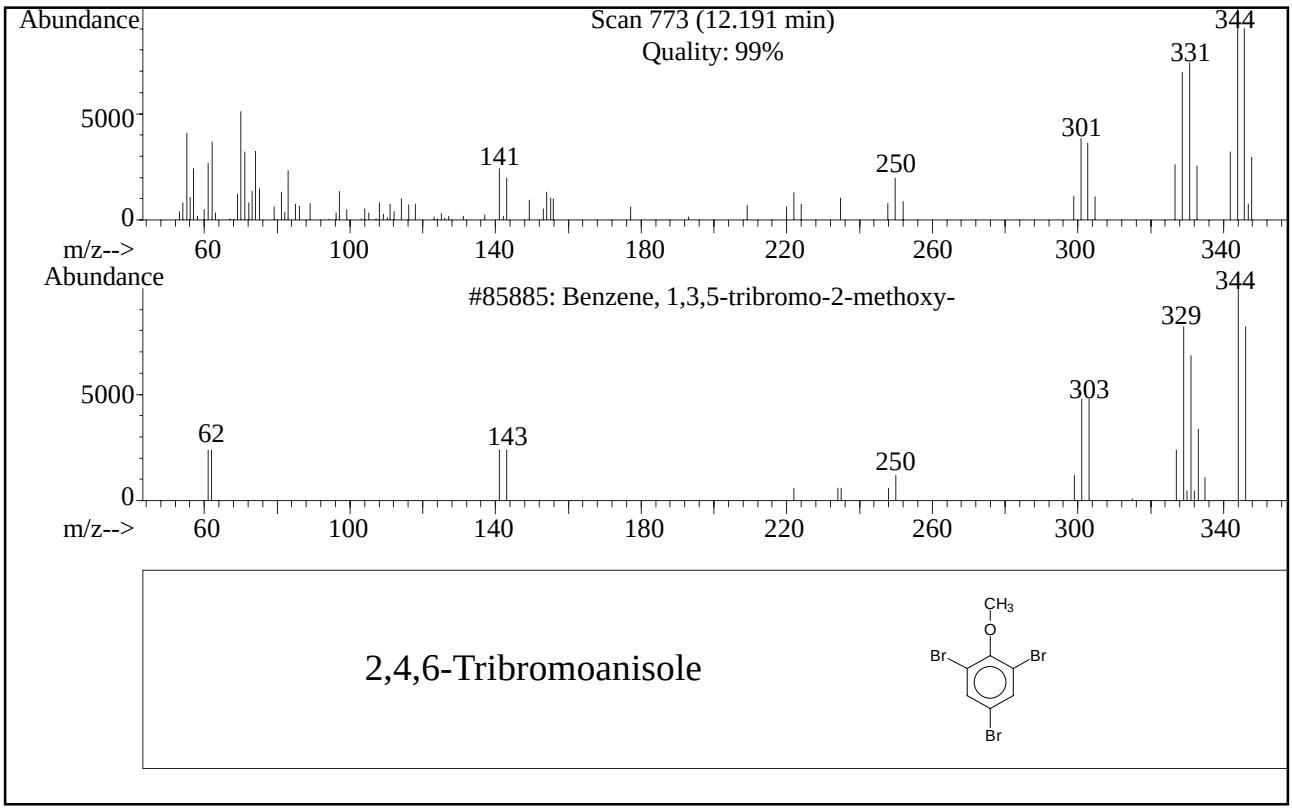

Figure 13. *Library search result for scan 733.*

The method of direct thermal analysis enabled us for the first time to analyse cork material without pretreatments like extraction and concentration. Therefore the material used for one analysis could be as small as 3 mg. The total time for one analysis did not exceed 1 hour compared to the extraction method which lasts at least 5 hours.

Due to the low amount of sample necessary for the analysis we were able to divide one cork stopper in several parts (**Figure 14** and **b**, **Table I**) and so we could find out, that the distribution of the Anisole and Phenol is different within one cork stopper. In that part of the cork where it was not extracted by the wine, a clear gradient can be observed rising on from the inner part (young, nearest to the tree) to the outer part. This indicates the environmental influence on the formation and presence of the tainting compounds. In the lower and middle part of the cork stopper the wine obviously has extracted the Anisole and the Phenol from the cork and therefore has to be regarded as "corky", an often observed and undesired off-flavour in wine.

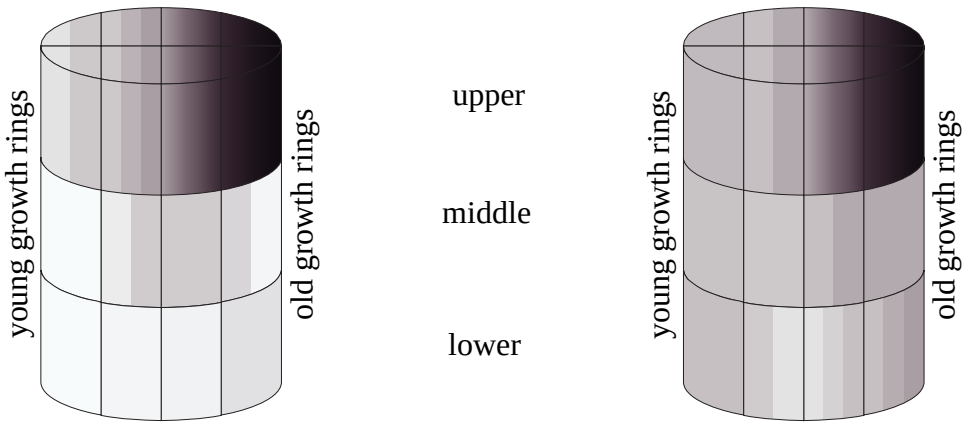

Figure 14. *Distribution of 2,4,6-Trichloroanisole (left) and -phenol (right) in cork stopper.*

growth ring age / part of cork	1-5 (years)	6-10 (years)	11-14 (years)	15-19 (years)
upper part	3104 / 4174	8663 / 3914	13692 / 6468	43961 / 24268
middle part	398 / 3759	3326 / 2807	7633 / 5228	790 / 5733
lower part	505 / 4087	842 / 2071	1917 / 1271	4493 / 6331

units = area-counts per mg sample 2,4,6-Trichloroanisole / 2,4,6-Trichlorophenol

Table I. *Distribution of 2,4,6-Trichloroanisole and -phenol in cork stopper.*

The comparison of cork stoppers from a spoiled and an unspoiled wine of the same origin (**Figure 15** and **16**) demonstrates this effect and at the same time confirms that the higher concentrations of 2,4,6-Trichloroanisole are to be found in the older corkcells at the surface of the tree.

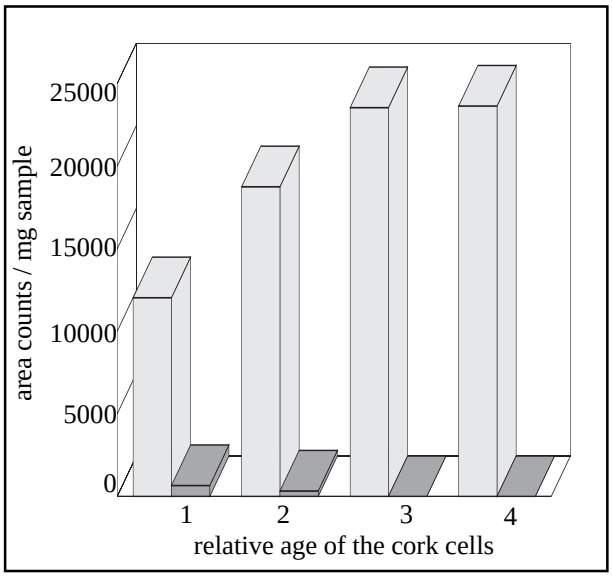

Figure 15. *Concentration of 2,4,6-Trichloroanisole in a corky (light grey) and a neutral (dark grey) cork dependent from the age of the cork cells.*

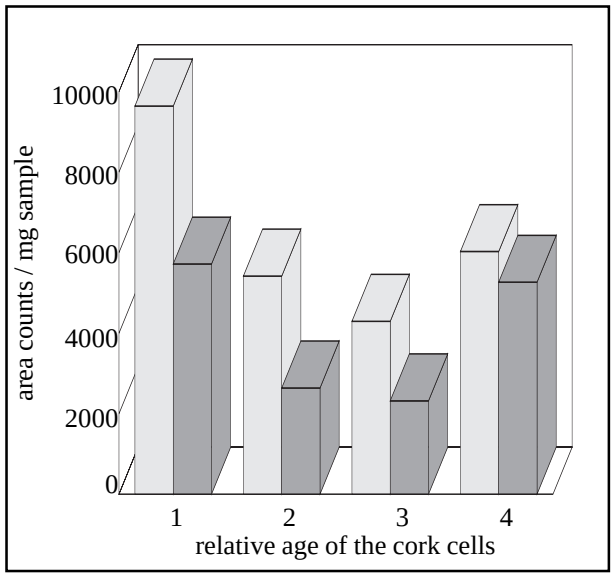

Figure 16. *Concentration of 2,4,6-Trichlorophenol in a corky (light grey) and a neutral (dark grey) cork dependent from the age of the cork cells.*

Conclusion

The method of direct thermal analysis enables us to analyse volatiles in solids without any sample pretreatment. It is very quick, reproducible and sensitive.

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