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Advances in the Capillary Gas Chromatographic Analysis of Beverages using PTV Injection combined with Ancillary Sample Introduction Systems

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ABSTRACT

The sources of compounds that produce desired flavors and undesired off-flavors in alcoholic and non-alcoholic beverages are the raw materials used in their production and the production process itself. There are typically hundreds of compounds present in a beverage, and the concentrations of these compounds varies enormously. This means that analytical techniques not only have to be suited to these concentration levels, but they also must be able to handle the complexity of the matrix.

This note will outline some strategies for beverage analysis resulting from recent technology advances in sample introduction techniques such as large volume injection, thermal desorption, thermal extraction and large volume (dynamic) headspace. These techniques offer significant advantages in establishing improved product authenticity fingerprints and lower detection limits. They are also useful for determining production related problems, such as off-flavors deriving from packaging materials.

Introduction

Temperature programmed sample introduction (or PTV injection) was originally developed and applied to the introduction of large volumes of biomedical samples by Vogt and co-workers [1,2]. In 1981 Schomburg [3] and Poy et. al. [4] demonstrated that the technique of cold split/splitless injection offers many advantages versus hot injection methods by showing greatly reduced discrimination of less volatile compounds. Quantitative performance of PTV injection turned out to be comparable to on-column injection, but without the undesirable effect of column contamination by sample residue.

Using the PTV as an enrichment and trapping device, and combining it with ancillary sample introduction systems, can greatly extend an analytical system's applicability.

Large Volume Injection

Large volume injection into capillary columns requires separation of the solvent from the analytes before they enter the column. This is necessary in order to avoid solvent flooding, column phase damage and analyte peak deformation [5]. This can be achieved by using the „solvent vent" mode of the PTV. In this mode, the sample is introduced slowly into the PTV liner with the split vent open, and with an inlet temperature below the boiling point of the solvent. After a certain period of time, the split vent is closed, and the analytes remaining in the liner after solvent elimination are transferred to the column in the splitless mode.

A fundamental study of solvent elimination, carried out by Staniewski and Rijks [6], has led to a formula from which the parameters for this process can be easily pre-calculated as a function of liner temperature, solvent type, purge gas flow and inlet pressure.

The example chosen here shows the total ion chromatogram of a large volume injection of a Kaltron extract of wine made from Morio-Muskat grapes [7]. Many compounds from wine aroma can be determined with this simple, fast, and at the same time, gentle (and therefore artifact free) sample preparation /enrichment method. The GC system is not contaminated with low volatility or non-volatile compounds (glycerine, sugar, dicarbonacids, dyes, etc.) which is unavoidable when injecting the wine directly. In addition, the capillary column is protected from large amounts of water.

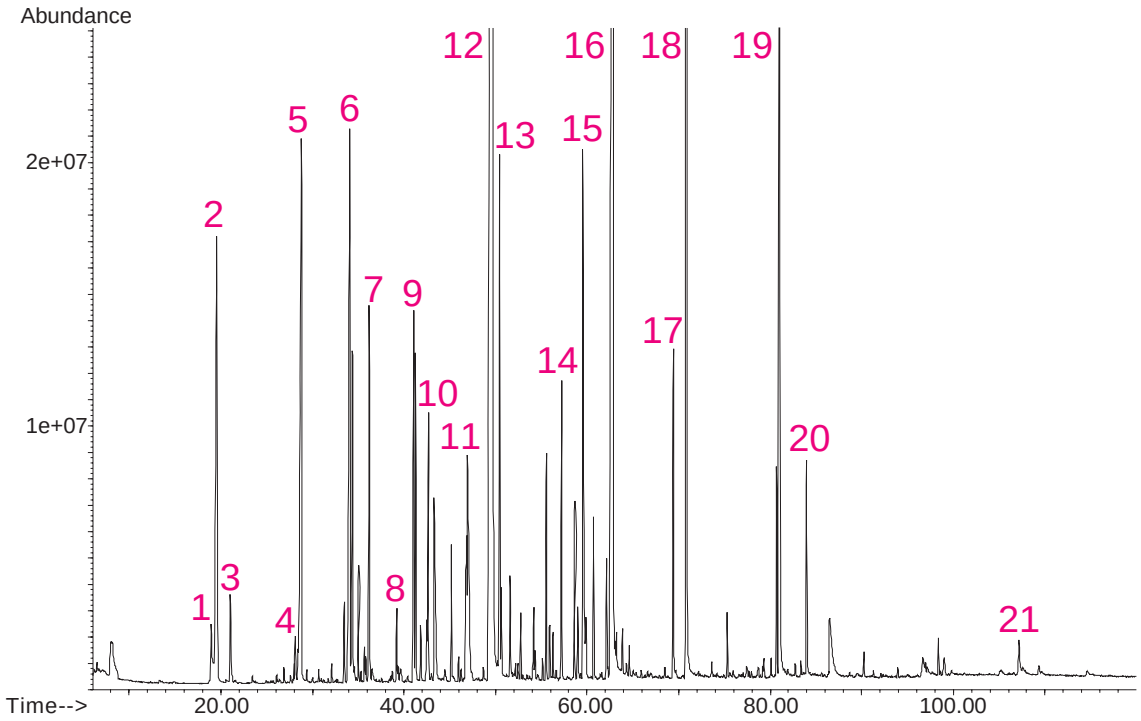

Figure 1. Total ion chromatogram of a large volume injection of a Kaltron extract obtained from a wine of the Morio-Muskat grape („Fingerprint"-chromatogram).

Table I. List of compounds.

No.	Compound	No.	Compound
1	2-Methyl-1-butanol	12	Diethyl Succinate
2	3-Methyl-1-Butanol	13	α-Terpineole
3	Ethyl Caproate	14	Phenyl Ethyl Acetate
4	Ethyl Lactate	15	Caproic Acid
5	Hexanol	16	2-Phenyl Ethanol
6	Ethyl Caprylate	17	Diethyl Malonate
7	trans-(f)-Linalool Oxide	18	Caprylic Acid
8	3-OH-Ethyl Butyrate	19	Capric Acid
9	Linalool	20	trans-Geranylic Acid
10	Acetoine	21	Myristic Acid
11	Ethyl Caprate		

Analysis Conditions.

MPS: 25 µl, at 20 µl/min
PTV: 1 min solvent vent (80 mL/min), splitless (1 min)
10°C (1.5 min), 12°C/s, 250°C (10 min)
Column: 60m HP-InnoWax (HP), d_i= 0.25 mm, d_f= 0.25 µm
Pneumatics: He, P_i= 24 psi
Oven: 40°C (1 min), 2°C/min, 240°C (20 min)

Headspace Injection

Static headspace injection is a valuable technique for determination of trace volatile compounds in food and beverages. An initial drawback was the need to use split injection to sufficiently focus the analytes at the head of the capillary column when injecting large volumes of headspace vapor. The necessity of using split injection limited the sensitivity of the technique.

Using the cooling feature of a PTV inlet offers an elegant means of obtaining the cryogenic focussing necessary for large volume headspace injection. In addition, the PTV liner can be packed with various adsorbents, which act as short pre-columns, that further contribute to the system's focussing capability.

In this case, a gas-tight autosampler syringe to provide a totally inert sample path has replaced the headspace transferline. For injection, the sample is drawn from a heated headspace vial into the heated syringe and injected into the pre-cooled PTV with the split vent open. After single or multiple injections, the system then switches to splitless mode and the PTV is heated to transfer the analytes of interest to the column.

This technique is demonstrated with an example of headspace GC-SCD monitoring of low volatile sulfur compounds during fermentation and in wine [8]. Very low levels of sulfur compounds give wines their distinctive aroma, but in higher concentrations they can create unappealing flavors.

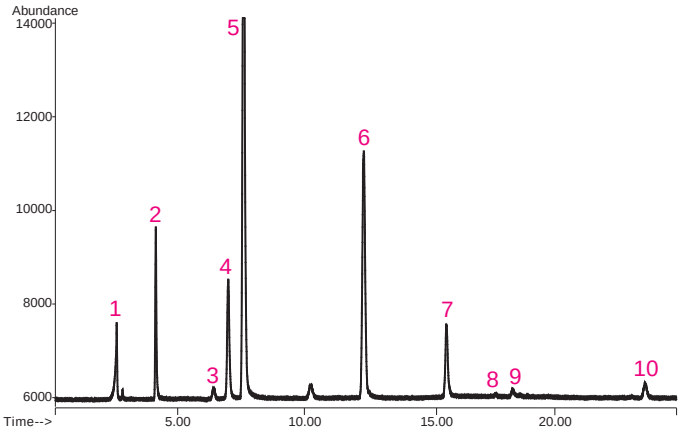

Figure 2. Sulfur trace of a 1996 Riesling wine with off-flavor (wine 1).

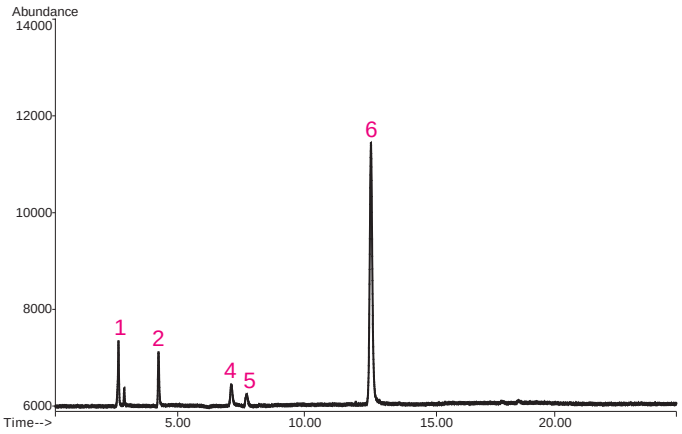

Figure 3. Sulfur trace of a 1996 Müller-Thurgau wine without off-flavor (wine 2).

Table II. List of compounds.

No.	Compound	(µg/l) in wine #1	(µg/l) in wine #2
1	Hydrogen Sulfide	7.2	4.2
2	Methanethiol	9.0	2.9
3	Ethanethiol	2.1	
4	Dimethyl Sulfide	13.0	2.1
5	Carbon Disulfide	17.9	1.3
6	Ethyl Methyl Sulfide (IStd)	30.0	30.0
7	Thioacetic Acid Methyl Ester	53.4	
8	Dimethyl Disulfide		
9	Thioacetic Acid Ethyl Ester		
10	Diethyl Disulfide	4.1	

Analysis Conditions.

MPS:	5x1000 µl (headspace) syringe = 60°C incubation = 60°C (45 min)
PTV:	25 mg Porapack Q, 80/100 mesh purge flow = 50 mL/min, splitless (8 min) -60°C, 12°C/s, 180°C (8 min)
Column:	30m SPB-1 (Supelco), d_i= 0.32 mm, d_f= 4.0 µm
Pneumatics:	He, P_i= 6.4 psi
Oven:	35°C (5 min), 10°C/min, 180°C (8 min)
Detector:	SCD (Sievers)

Thermal Desorption / Thermal Extraction

Both detection limits, and the functionality of the PTV can be further enhanced by combining it with a thermal desorption unit, which itself can be temperature programmed. In this approach, an adsorption tube containing the analytes of interest obtained from large volume purge and trap sampling, is placed in the thermal desorption unit, which is connected directly to the PTV. The thermal desorption oven is then heated using a temperature program to desorb the components which are then cryogenically focused in a cooled PTV liner. After thermal desorption is complete, the PTV is heated to transfer the analytes of interest to the column in either split or splitless mode.

An interesting variant of this approach is to place the sample (usually a solid) directly in an empty thermal desorption tube and purge the volatile compounds into the PTV for concentration by cryogenic focussing. In this dynamic headspace approach, the sample is kept at a low temperature, but purged for an extended period of time to transfer the maximum amount of volatile compounds to the cooled PTV.

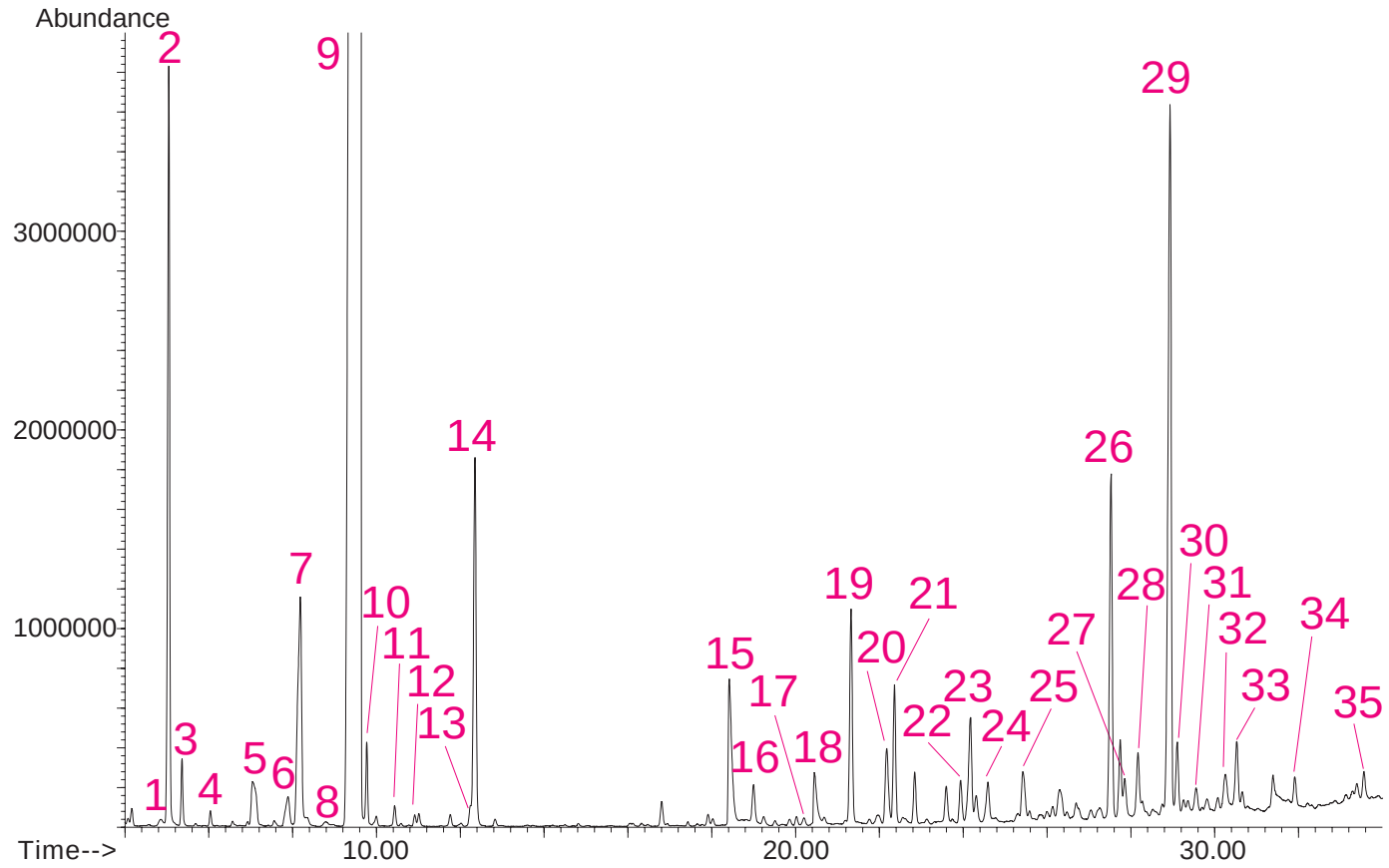

Figure 4. Total ion chromatogram of volatiles from 1 ml freshly squeezed orange juice.

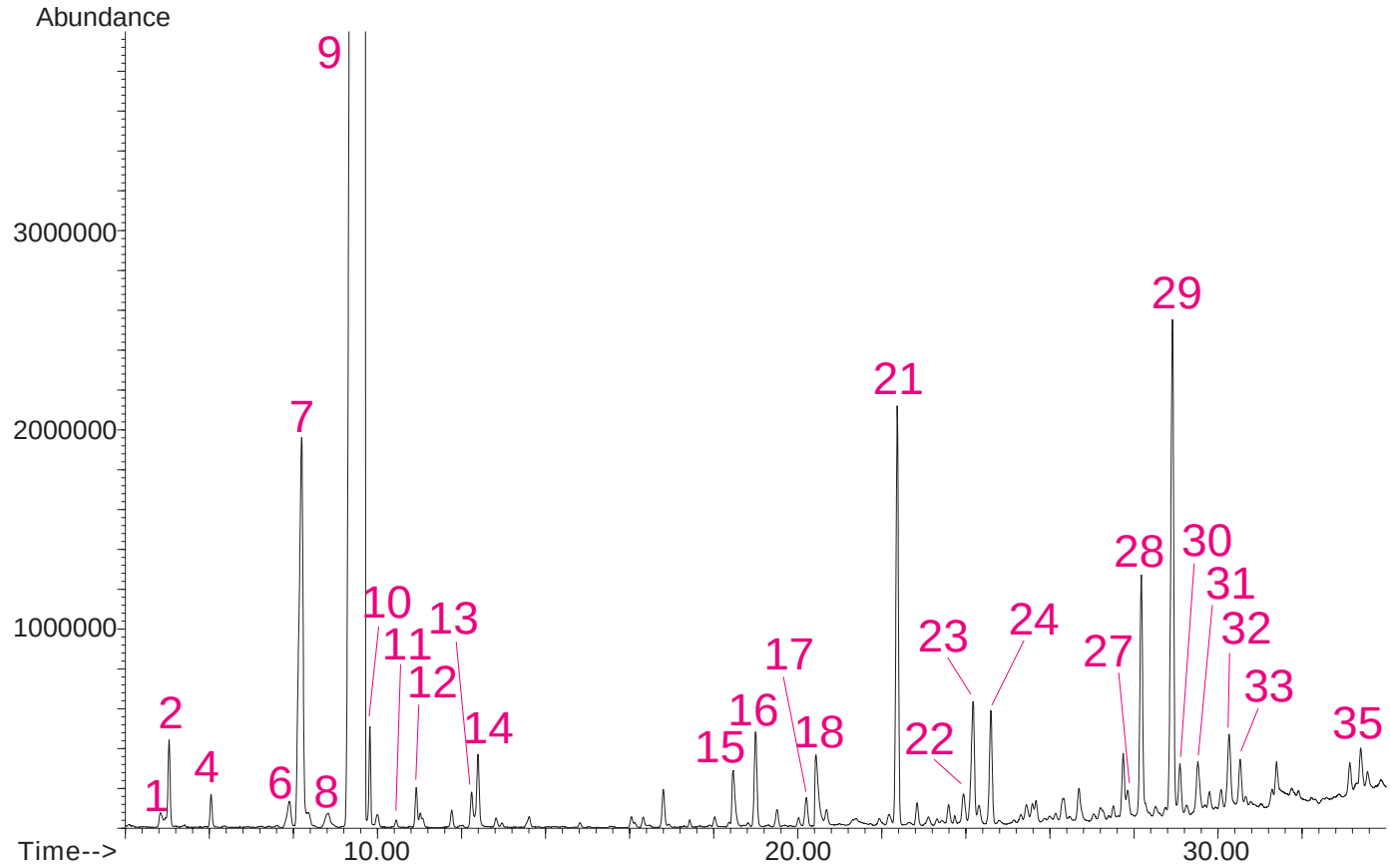

Figure 5. Total ion chromatogram of volatiles from 1 ml commercial orange juice.

Fruit juices can be very complex, containing several classes of compounds like terpenes, esters, alcohols, etc. Traditional methods of analysis require time consuming and cumbersome sample preparation techniques such as solvent extraction, or incomplete recovery methods such as classical purge & trap techniques, which recover only very volatile and non-polar compounds.

The technique of thermal extraction overcomes these problems by thermally extracting all volatile compounds onto an adsorbent-filled tube, followed by thermal desorption and transfer of analytes to the column. This technique requires minimal sample preparation, and significantly reduces overall analysis time, without sacrificing data quality.

Table III. List of compounds.

No.	Compound	No.	Compound
1	α-Pinene	19	Ethyl-3-Hydroxy Butyrate
2	Ethyl Butyrate	20	2,3-Butanediol
3	Ethyl-2-Methyl Butyrate	21	Linalool
4	Hexanal	22	Hexadecane
5	Sabinene	23	1,2-Propanediol
6	δ-3-Carene	24	Terpinene-4-ol
7	Myrcene	25	Butyric Acid
8	α-Terpinene	26	Ethyl-3-Hydroxy Hexanoate
9	Limonene	27	β-Selinene
10	β-Phellandrene	28	α-Terpineol
11	Ethyl Caproate	29	Valencene
12	γTerpinene	30	α-Selinene
13	α-Terpinolene	31	Carvone
14	Acetoine	32	δ-Cardinene
15	Acetic Acid	33	7-epi-α-Selinene
16	Furfural	34	Nerol
17	α-Copaene	35	Geraniol
18	Formic Acid		

Analysis Conditions.

TE:	100°C
TDS:	Tenax TA, 35/60 mesh 20°C, 60°C/min 250°C (10 min)
PTV:	purge flow = 50 mL/min, split 1:20 -150°C, 12°C/s, 280°C (5 min)
Column:	30m DB-Wax (J&W), d_i= 0.25 mm, d_f= 0.5 µm
Pneumatics:	He, 1 mL/min
Oven:	60°C (1 min), 8°C/min, 220°C (20 min)

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