

THIRTY YEARS OF COFFEE CHEMISTRY RESEARCH

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1. INTRODUCTION

In the 60s gas chromatography was on the brink of a breakthrough; my first job was to elucidate the secrets of the coffee aroma. But the equipment of those days was still not sufficiently well developed. It took exactly 30 years before we had satisfactory results.

Good physico-chemical knowledge was needed when we had to evaluate a completely new and imaginative process for caffeine removal from green coffee beans: This was the decaffeination by supercritical carbon dioxide; such a compressed gas has the same dissolving power like other lipophylic solvents, as for example methylene chloride, ethyl acetate etc. My team had to carry out the first experiments on lab scale, and to make a chemical assessment of the product. By the way, we further applied this knowledge to file patents on extraction of spices, tea, cocoa, hops and nicotine from tobacco (Hubert and Vitzthum, 1978). Several processes are worldwide in use today.

In the 70s, the first real work on coffee aroma started using more sophisticated instrumentation; we identified some 180 new volatiles in green and roast coffee (Vitzthum, 1975; Vitzthum and Werkhoff, 1975). Ten years later the first practical successful work on coffee aroma was, however, not the identification of good aroma, but the off flavors in coffee end of the 80s. The less off flavors—the more good coffee flavor you may find.

In parallel we helped to develop a new patented Instant Coffee process. In contrast to the commercial process, now the extraction percolators were chosen to be much shorter, their number was doubled, and the grind size of the roast coffee was decreased; together with a special aroma management, a more roastcoffee-likeness could be achieved (Vitzthum and Koch, 1991).

2. COFFEE AROMA

Coffee aroma and flavor determine about 80% of the quality of a roast coffee beverage. As the Coffee Industry always is obliged to offer the best quality and convenience at an optimal price, a considerable amount of money—especially in the major Companies—is spent for coffee aroma research.

What is Coffee Aroma?

Green coffee beans from the tree and after processing, do not yet have the color nor the aroma of roast beans. Both are formed during the roasting process—normally at 210° Celsius for 6–10 mins. The coffee oil, which comprises about 10% of the roast beans, carries most of the coffee aroma. The latter is concentrated in 0,1% by weight of volatile compounds. These substances can be isolated by steam distillation, and extracted therefrom by lipophilic solvents like ether and pentane. The resultant concentrate is highly unstable and rapidly turns from a colorless liquid to an orange and dark red color, due to degradation reactions; it has to be stored under frozen conditions.

Historically it should be mentioned that—even before the invention of gas chromatography—well known scientists like Nobel Prize winners REICHSTEIN, STAUDINGER and WOODWARD (Reichstein and Staudinger, 1926; Prescott and Woodward, 1937), made the first identifications of coffee aroma compounds such as furfurylmercaptan and guaiacols.

By using more and more sophisticated techniques, such as GC/MS, the number of characterized compounds in roast coffee has been increased to more than a thousand by today. As in practice a real authentic coffee aroma compound was no longer being found, it became evident that it does not make sense just to increase numbers of compounds found.—A new concept, developed at the end of the 80's, showed a new approach to aroma characterisation: that was the search for sensory active key aroma compounds, also called character impact components, which clearly contribute to the smell or odour of a food aroma (Schmid and Grosch, 1986).

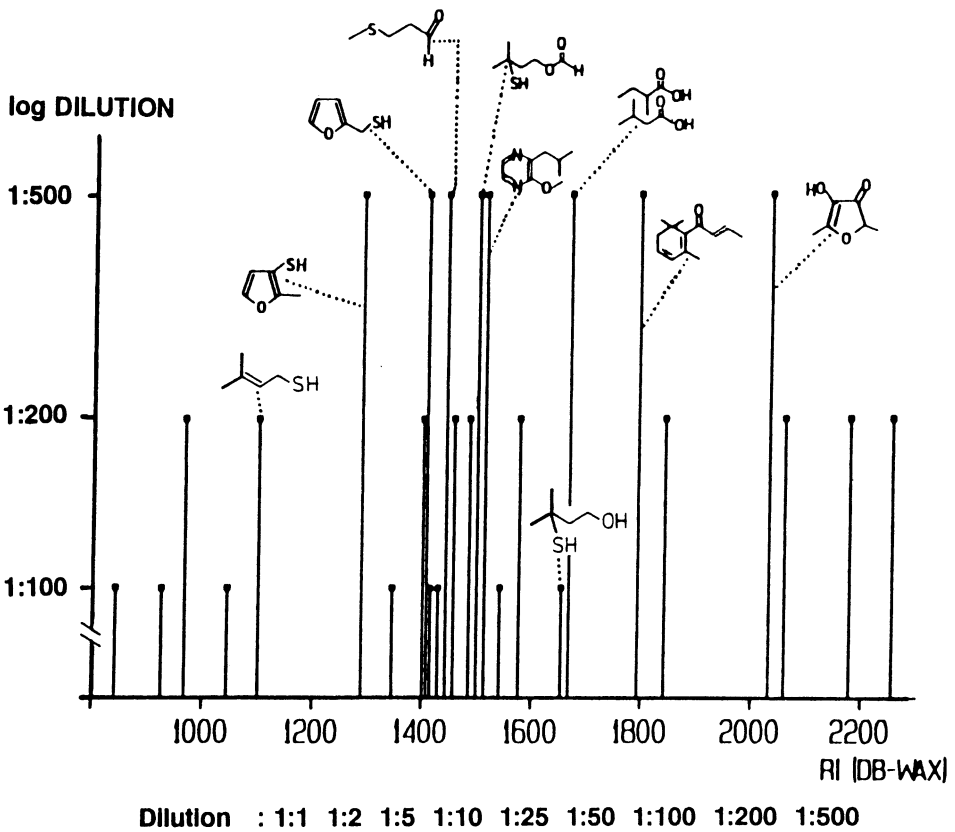
Here I shortly have to interrupt: you may ask, is it not the aroma alone but the taste which makes coffee the preferred beverage? That is only partially true: non-volatile taste components only determine sourness and bitterness; the characteristic coffee aroma/smell comes from the volatile compounds and the perceived flavor of the coffee beverage in the mouth, which you also do recognize in the nose by smelling because the volatile compounds from the surface of the coffee liquid on the tongue will go to the same organoleptic receptors in the bulbus olfactorius in the nose via the retronasal connection.

The new way in Coffee Aroma Research was to look for the active smelling compounds in the aroma complex (Schmid and Grosch, 1986). This was achieved by smelling at the outlet of a gas chromatographic column.

Many volatile compounds of the complex do not smell; those which do smell have to be further examined. But what to do with these highly different odors, that do not smell like coffee? The relative aroma importance of single volatile components can be determined by the so-called aroma dilution technique.

After each injection into the GC the aroma concentrate is diluted 1 : 5 or 1 : 10. By every further dilution, certain compounds were eliminated from sensory detection at the column outlet; only the most active smelling volatiles would remain under the last 5–10 at a certain end dilution (Fig. 1).

They were the very substances that overwhelmingly contribute to the real coffee aroma, perceptible by the human nose. Also it became possible to discriminate between



Aromagram of a total aroma fraction of roast Colombian coffee

Figure 1. Aroma dilution analysis of a Columbia coffee aroma fraction.

good coffees, and those containing less desirable or negative, so-called off flavors; a discrimination between coffees of different origins could be achieved as well.

2.1. Experimental Techniques

There are preferably two isolation and clean-up procedures in use: the so-called LIKENS-NICKERSON technique and the High Vacuum distillation method according to GROSCH. The Likens-Nickerson, also called SDE (steam distillation extraction) is already well known. The High Vac distillation apparatus consists of a rotatory evaporator, connected to a high vacuum pump via chilled traps, in order to recover the light volatiles (Fig. 2).

The whole procedure from clean-up until identification comprises the following:

- ISOLATION
- CONCENTRATION
- FRACTIONATION
- IDENTIFICATION
- SYNTHESIS

Syntheses could be necessary for authentic proof of unknown compounds.

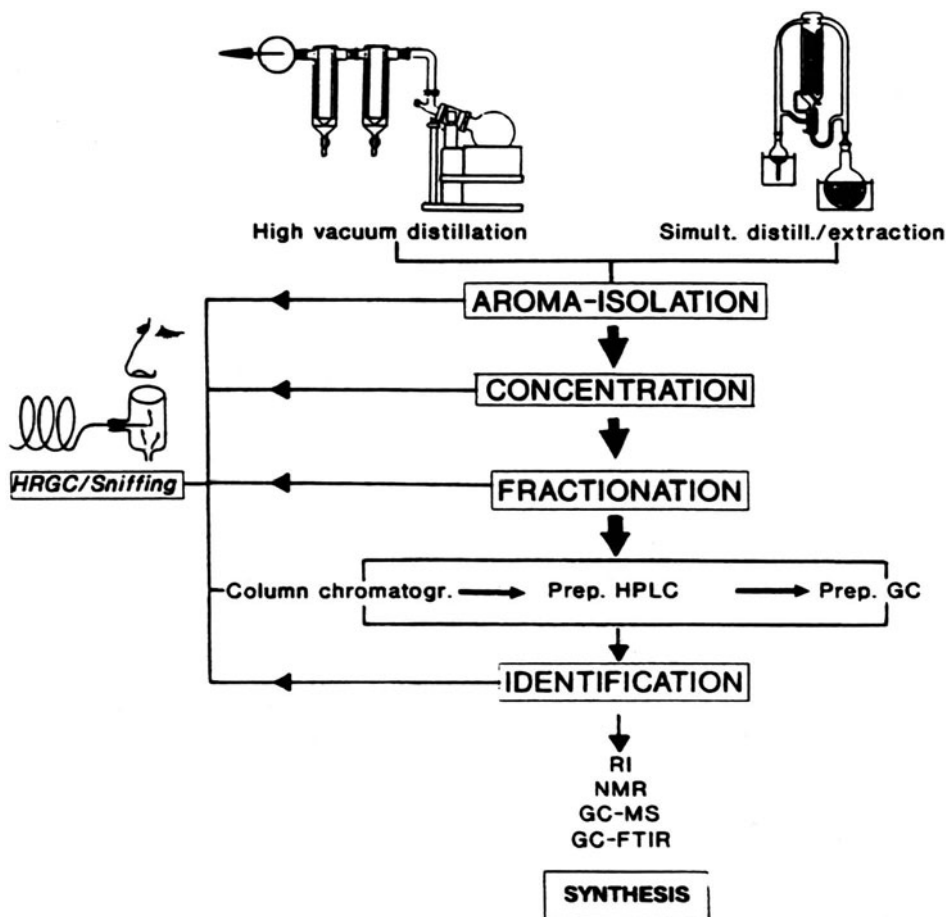


Figure 2. Clean-up procedures for the volatiles of green and roast coffee.

Parallel with the IDENTIFICATION steps a sniffing at the outlet of the capillary column is carried out in order to characterize the active smelling compounds by name.

In answer to the question what modern instrumentation is used:

Besides several gaschromatographs, the following combinations may be used:

GC MS quadrupol

GC MS ion trap (modern version)

double focussing high resolution tandem GC-MS

(BEQ arrangement)

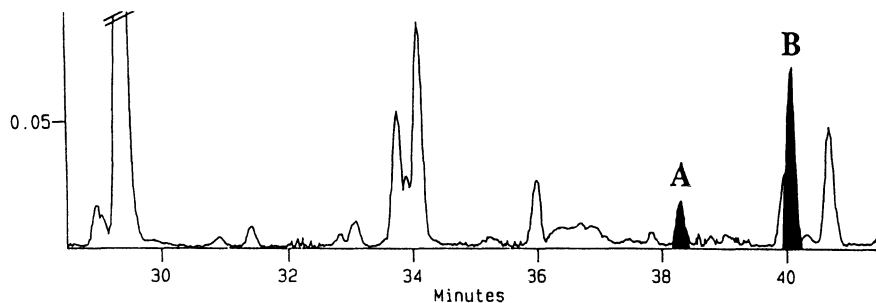
The tandem MS and one of the modern ion trap versions today replaced the tedious 2-dimensional gaschromatography of end of the 80's (Becker *et al.*, 1987) due to their high sensitivity and flexibility (Holscher *et al.*, 1995). Many of the interesting aroma key compounds are present in very small amounts; as they sometimes can be hidden under other major peaks a preparative capillary gaschromatography step has to be used for further selective enrichment.

In the case of isomer characterization, infrared spectroscopy and nuclear magnetic

resonance spectroscopy must be used for authentic proof. NMR is not sufficiently sensitive but the new FT-IR techniques can help, especially the GC-FTIR TRACER version (Fig. 3), analyzing the solid sample.

NMR, of course, is the top tool for the authentic confirmation of the molecular structure. But unfortunately heretofore 100 times higher amounts of the substances are needed, than normally are isolatable by one GC run. Such quantities only can be obtained by repetitive preparative capillary gas chromatographic and/or preparative HPLC isolation.

Electron resonance spectroscopy may be used in such cases where one would like to study the roast process and investigate any free radical formation (Morrice *et al.*, 1993). This might have an influence on the aroma freshness stability of roast coffee.



Cut from a Gram-Schmidt chromatogram and FTIR-spectra of isomeric 2,4-decadienals

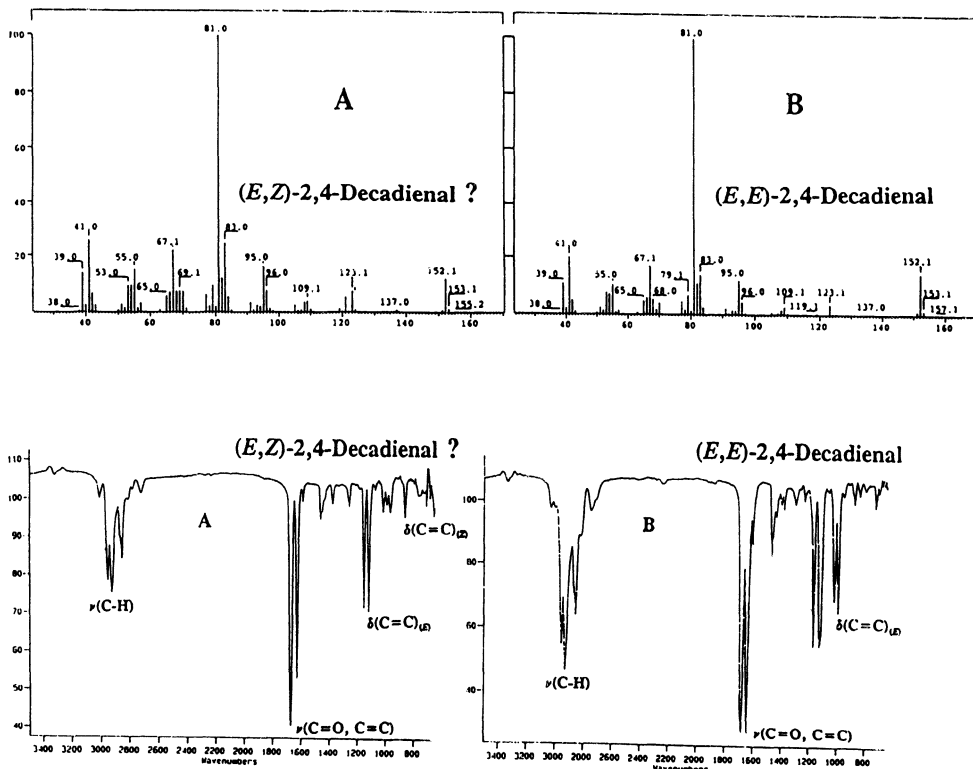


Figure 3. Characterization of 2,4-decadienals by GC-FTIR TRACER techniques.

2.2. Coffee Quality

How can the results from applying these techniques be used?

I would like to demonstrate typical applications. Table 1 shows the main factors that determine Coffee Quality:

Many of these criteria can be checked by the aforementioned techniques.

Off flavors, ARABICA/ROBUSTA distinction: Our first intention to look for "good coffee flavors" was interrupted by the more important identification of less desirable flavors; the lesser the content of such off flavors in a coffee blend, the better would be the quality. We could characterize "old crop" notes, peanutty flavors, transportation flavors (from jute bags), process off flavors, peasy notes in coffee from Ruanda, "stinker" beans, and two off-flavor compounds that attracted most our attention:

2-methylisoborneol in Robustas, and 2,4,6 trichloroanisol in Rioy Arabicas from Brazil. Whereas the latter was elucidated by NESTLE RESEARCH (Spardone and Liardon, 1987), we were particularly interested in methylisoborneol (Table 2);

This compound was one which we found (Vitzthum *et al.*, 1990), representing some 60–70% of the less desirable aroma of Robusta coffee.

Table 1. Factors determining the coffee quality.

Influential Factors on Coffee Quality in Producer Countries

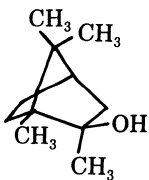
- o botanical varieties Arabica and Robusta
- o species, geographical origins
- o green coffee processing
- o off flavors

Influential Factors on Coffee Quality in Consumer Countries

- o transportation from producer country
- o blending
- o upgrading processes
- o roasting
- o packaging
- o staling

Table 2. Methylisoborneol (MIB) from Robusta coffee.

2-METHYLISOBORNEOL (MIB)



| | |
|--------------------------|------------------------------|
| Odour threshold (water): | 2.5 ng/liter |
| Odour character : | |
| (pure substance) : | camphor-like |
| (diluted) : | musty, earthy, mouldy |
| MW : | 168.3 |
| M.P. : | 154 - 156°C |

Table 3. MIB distribution in Arabica and Robusta coffees.

| MIB in Various Roasted Robusta and Arabica Coffees (ng/kg Dry Matter) | | | |
|----------------------------------------------------------------------------------|------------|--------------------|----------------|
| ROBUSTA | MIB | ARABICA | MIB |
| Indonesia | 310 | Brazil | < 20 |
| Uganda | 185 | El Salvador | < 20 |
| Brazil Conilon | 120 | Colombia | < 20 |
| Ghana | 430 | Kenya | < 30 |
| Zaire | 240 | | |
| Ivory Coast | 200 | | |
| The Cameroons | 120 | | |

Robusta coffees are well known to those, who ever drank a typical coffee brew in France. MIB, which is how we abbreviate this compound, gives the coffee flavor, an earthy, tarry character. MIB is present only in very tiny amounts, even in Robustas. But due to its low threshold flavor level, it can be recognized sensorily at the outlet of a gaschromatographic column. Initially we had to use 2-dimensional GC-MS for quantification (Fig. 4).

Today, it is easier using HR-Tandem-GCMS with a deuterated internal standard (Bade-Wegner *et al.*, 1993) (Fig. 5).

The MIB content in Arabias is negligible (Table 3).

Reduction of the MIB content in certain Robustas by technical processing provides a more positive flavor, more like that from unwashed Arabica coffees (Becker *et al.*, 1989). However care must be taken not to generate new off flavors.

The trichloroanisol has an even lower threshold (Fig. 6).

In water, TCA has the lowest known threshold of all smelling compounds, known so far. You can recognize sensorily, already 50 femtograms in 1 l water. Brazil Rioy coffee has a medicinal, chloroform like, musty note. All trials to reduce TCA significantly have failed so far.

To our surprise, we detected TCA also in an African top quality Arabica from Kenya. This was strange, until we found out, that some farmers there had used a pesticide, that already contained TCA in the molecule (Holscher *et al.*, 1995) (Fig. 7). Immediately they abandoned use of that pesticide.

TCA also can be found additionally to MIB in certain Robustas, such as from the Ivory Coast.—Recently, we succeeded in the elucidation of the overfermented bean flavor from so-called “stinkers” (Bade-Wegner *et al.*, 1997). Stinker beans will be found in coffee blends from time to time and so give the beverage an intolerable fruity, rotten flavor (Fig. 8). There were found to be 3 responsible compounds, cyclohexanoic acid ethylester (CHEE) being the dominant one (Bade-Wegner *et al.*, 1997).

A summary of all off flavors is given in Table 4:

2.3. Coffee Characterization: Discriminant Analyses

Discrimination of species, origins: According to BOBILLOT and SCHIEBERLE, the flavor impressions from taste panels can be presented in form of a “star diagram” (Bobillot *et al.*, 1997; Schieberle and Hofmann, 1997) (Fig. 9);

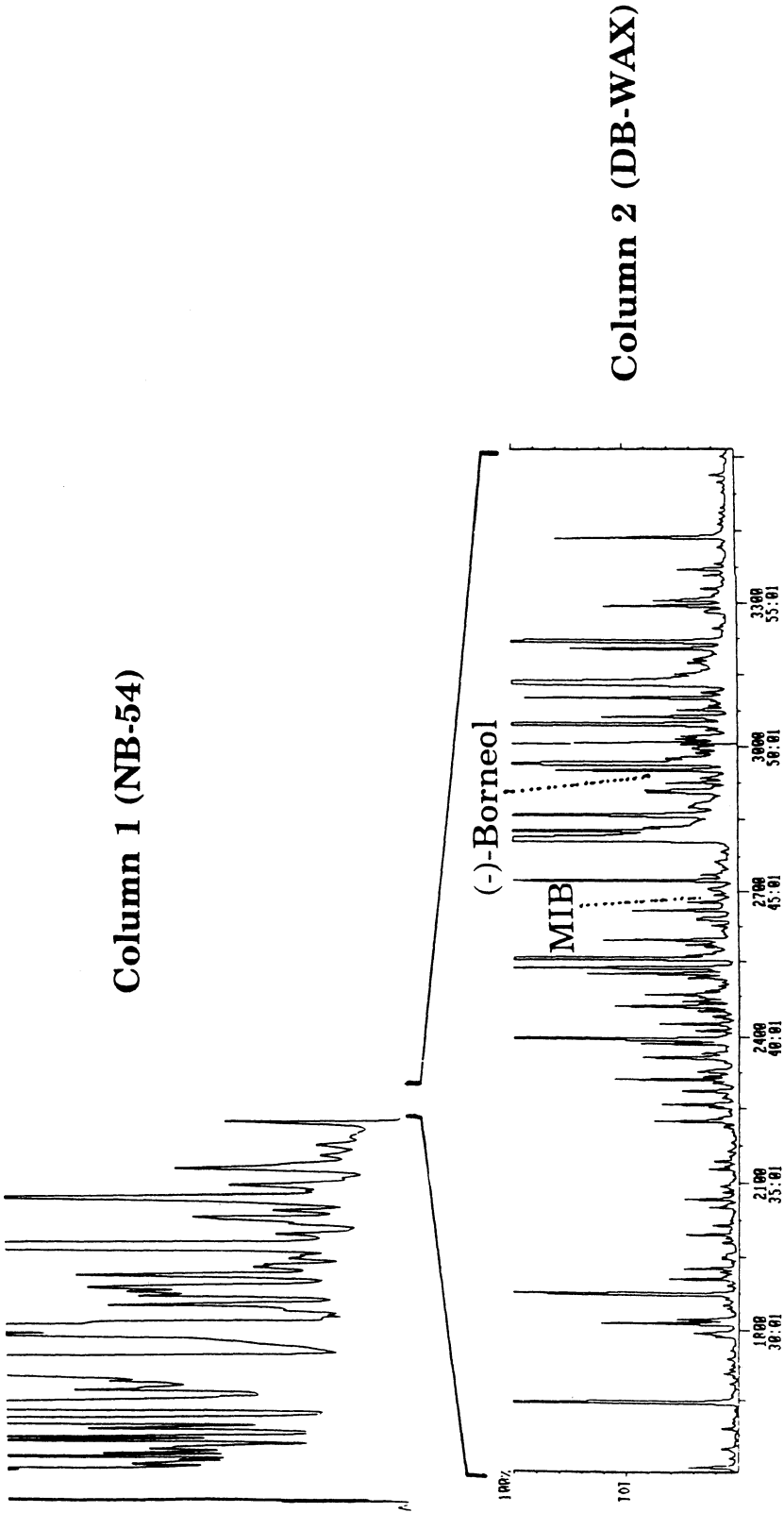
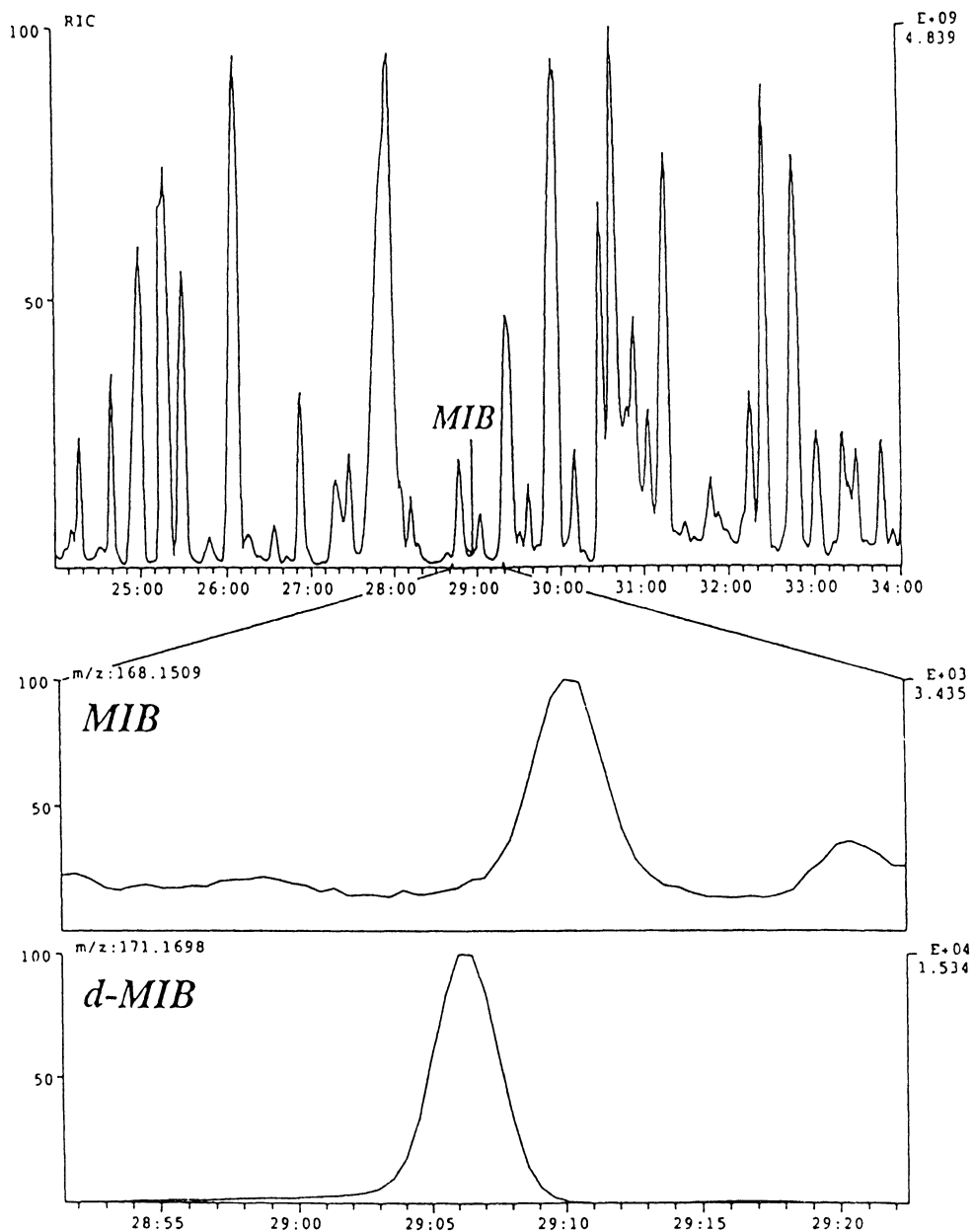


Figure 4. Identification of MIB in coffee by 2-dimensional GC.



Cuts from a total ion chromatogram and MID mass tracks of a subfraction of a roasted Indonesian Robusta aroma extract.

Figure 5. Quantification of MIB by HR-Tandem-GCMS adding deuterated MIB.

GC-Sniffing Chromatogram of a Green Brazilian "Rio"-Flavor Coffee

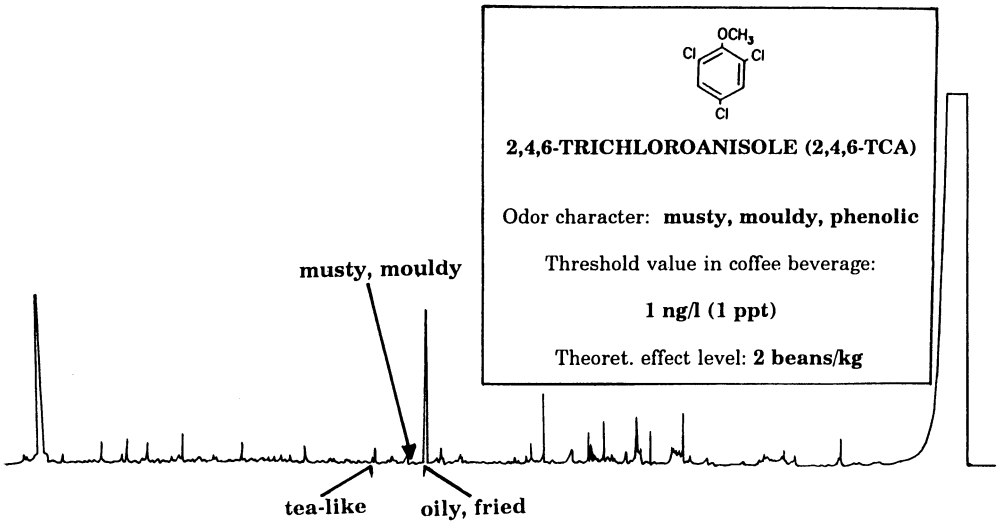
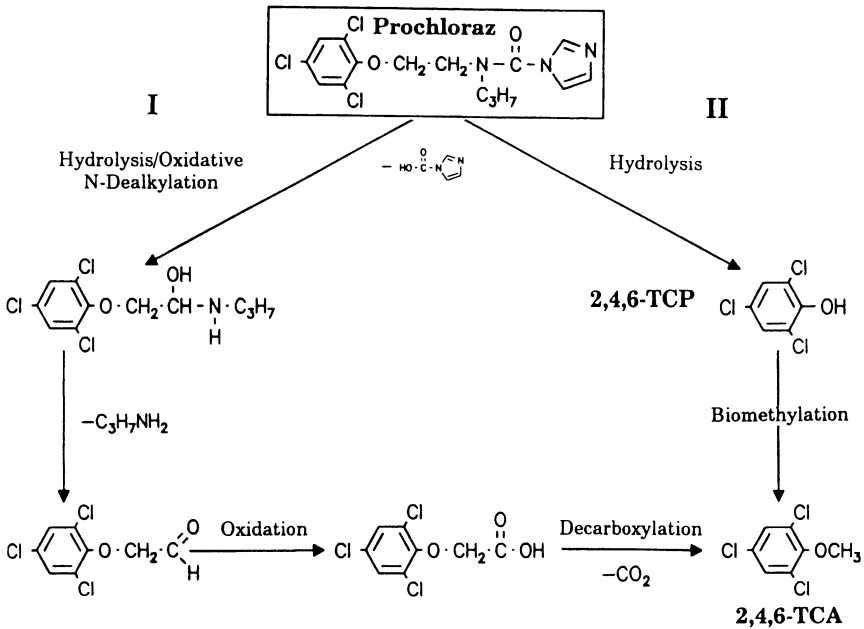


Figure 6. TCA in Brazilian Rio coffee (Spadone and Liardon, 1987).



Hypothetical degradation pathway of pesticide Prochloraz

Figure 7. Hypothetical degradation pathway of pesticide PROCHLORAZ.

Odourants associated with the over-fermented flavor defect.

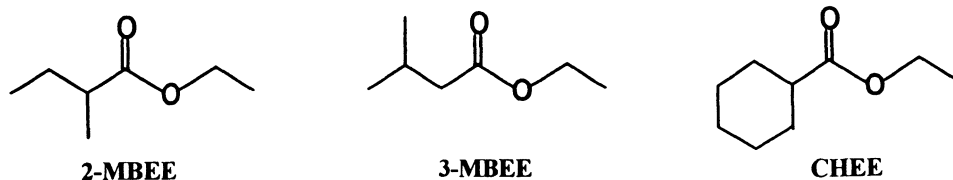


Figure 8. Compounds associated with the flavor of "stinker" beans.

Table 4. Off flavors to be found in some green raw coffees.

| <u>Off Flavor related Raw Coffee Volatiles</u> | |
|---------------------------------------------------------------------------|----------------------------------------------------------------------------|
| "Peasy" in Ruanda coffees | - 2-methoxy-3-iso-propylpyrazine |
| "earthy" key note in Robustas | - (-)2-methylisoborneol, |
| "musty, medicinal" note in Rio Brazil | - 2,3,6-trichloroanisole |
| "old crop" flavor | - unsaturated aldehydes |
| "peanutty" off flavors | - 2,4-(tr,tr)-Decadienal |
| process flavor | - β -damascenone |
| roast coffee staleness contributor | - hexanal |
| "stinker" beans | - 2- and 3-methyl butanoic acid ethylester, cyclohexanoic acid ethyl ester |
| "sack" off flavors in certain jute bags - sometimes in coffees from India | - mineral oils (phytanes) |

Notes such as roasted, burnt, cooked, caramel, green, earthy etc. can be profiled semiquantitatively on the axes of such a star. By attributing the corresponding key aroma chemicals to those axes, the diagrams can be quantified. These correlations can be established knowing the sensory terms of the key compounds, derived from GC-Olfactometry and taste panel assessments (Holscher and Steinhart, 1995) (Table 5).

The covered areas then will allow a distinction between different coffee species, for green coffee as well as for roast coffee. In a just completed research report, W. GROSCH, provided proof of the use of aroma compounds, as indicators for origin dependent aroma differences in Arabica coffees like those from Columbia, Brazil, Salvador, Ecuador and Kenya (GROSCH, 1998 pers. comm.).

Another possibility will be to use the quantitative data on key aroma compounds for discriminant analyses. Early experiments in this direction had been carried out by GIANTURCO in the late 60's (Biggers *et al.*, 1996) and LIARDON in the 80's (Liardon and Spadone, 1985). An example from us shows the discrimination of roast coffee beans possible with respect to freshness and botanic variety, based on head space profile analysis (Fig. 10) (Vitzthum *et al.*, 1991).

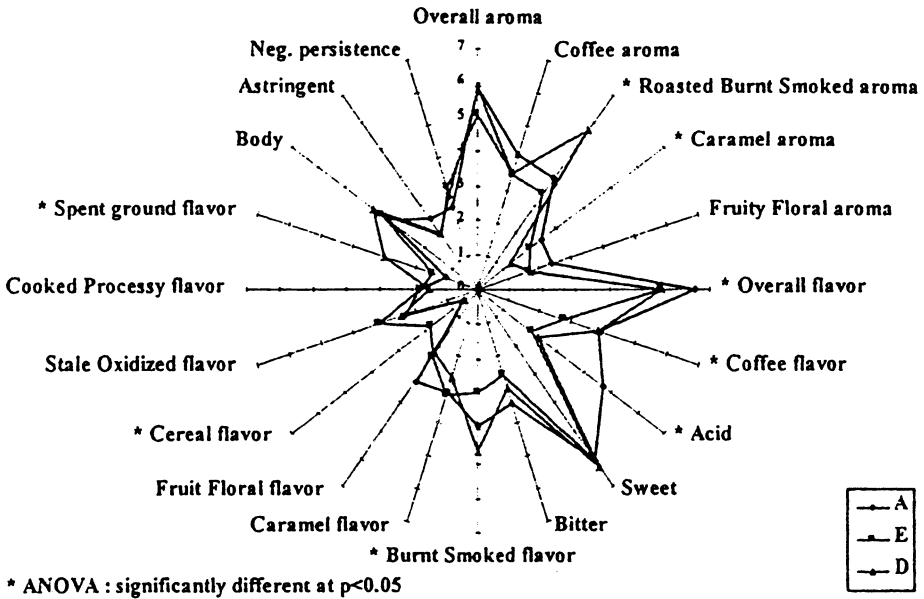
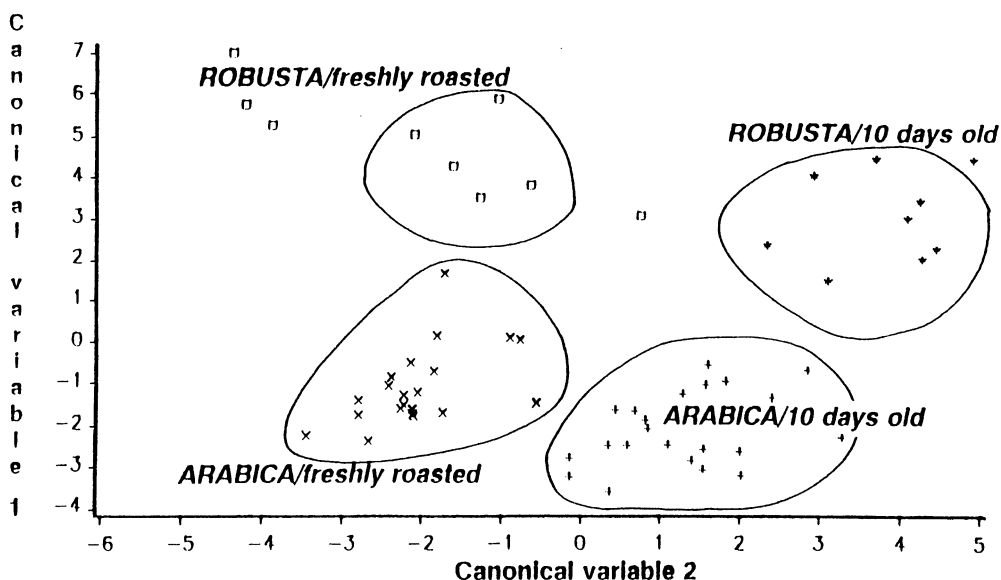


Figure 9. "Star" profile diagram of sensory impressions from coffee (Bobillot *et al.*, 1997).

Table 5. Sensory impressions from single green coffee volatiles by smelling at the outlet of a GC.

| GC-Olfactometry of a Green Coffee Aroma Extract. | | |
|--------------------------------------------------|----------------------------|----------------|
| Compound | Odor Description | Odor Intensity |
| n-hexanal | <i>green, oily</i> | + |
| n-heptanal | - | |
| (E)2-hexenal | - | |
| 1-octen-3-one | <i>mushroom-like</i> | + |
| (E)2-heptenal | - | |
| 3-methyl-2-buten-1-ol | - | |
| n-nonanal | <i>soap-like, metallic</i> | ++ |
| (E,E)2,4-hexadienal | - | |
| (E)2-octenal | - | |
| 2-methoxy-3-isopropylpyrazine | <i>peasy</i> | +++ |
| methional | <i>cooked-potato-like</i> | +++ |
| 1-octen-3-ol | - | |
| (E,E)2,4-heptadienal | - | |
| n-decanal | - | |
| (Z)2-nonenal | <i>metallic, tallowy</i> | +++ |
| benzaldehyde | - | |
| 2-methoxy-3-isobutylpyrazine | <i>bell-pepper-like</i> | +++ |
| (E)2-nonenal | <i>fatty, tallowy</i> | +++ |
| linalool | <i>flowery</i> | +++ |
| (E,Z)2,6-nonadienal | <i>cucumber-like</i> | +++ |
| phenylacetaldehyde | <i>honey-like</i> | +++ |
| 2,4-nonadienal, isomer | <i>metallic, tallowy</i> | + |
| 2-methyl butyric acid | <i>fermented</i> | + |
| 3-methyl butyric acid | <i>sweaty</i> | +++ |
| (E,E)2,4-nonadienal | <i>geranium-like</i> | ++ |
| (E,Z)2,4-decadienal | <i>metallic, tallowy</i> | + |
| (E,E)2,4-decadienal | <i>fried, oily</i> | +++ |
| β -damascenone | <i>fruity, tea-like</i> | +++ |

+: weak; ++: strong; +++: very strong

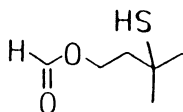


Canonical discriminant analysis: Discrimination of roast coffee beans with respect to botanical variety and freshness based on head-space-profile analysis

Figure 10. Canonical discrimination of fresh and 10 days old Robusta and Arabica roast coffees.

Roasting: Although green (raw) coffee beans have a certain aroma,—sufficient for distinction of species—the desirable real coffee aroma and color only is developed by roasting of the green beans. There will be a decrease in content of proteins, sucrose, phenolic acid esters, and so-called chlorogenic acids. The brown compounds, called melanoidins, with as yet unknown chemical structure and negligible taste, will be formed. Well-known important volatile flavor substances like pyrazines, phenols, Strecker aldehydes, enol-oxo compounds and important sulfur substances also will be generated (Parliament and Stahl, 1995). The important sensory notes roasted (pyrazines), rubbery (some thiols), woody (nonenal), burnt (guaiacols), and “in-pack aroma” (methanethiol) stem from them. Many of the key odorants, however, are already present in the green beans, and most of the off flavors are not affected by roasting.

One of the key aroma notes, that markedly contributes to “roast coffee-likeness” is a compound that we called MMBF, the abbreviation of 3-mercapto-3-methyl-butylformate (Holscher *et al.*, 1990) (Fig. 11). The pure compound does not smell like coffee; it has a blackcurrant like, catty note. Only when in great dilution in a coffee beverage—especially if prepared from soluble coffee—does MMBF justify the term “roast coffee likeness”.



3-Mercapto-3-methyl-butyl formate

Figure 11. MMBF: a “roast coffee like” note in coffee.

2.4. Aging, Staling of Coffee

Twenty years ago, we reported on a simple head space method in order to characterize the “roast freshness” of roast coffee. We then analyzed the quotient of 2-methylfuran/2-butanone, that we called aroma index M/B, in the headspace over ground coffee beans (Fig. 12).

Though these compounds do not sensorily represent the aging of coffee, they are correlated with it and may be used as indicator compounds (Clarke, 1986). This technique is useful for coffee of known blend and roast degree, to follow the degradation over days and weeks; it cannot be used for coffees stored in vac packs or cans. From the further research it was realized to better store roast coffee in a refrigerator or optimally in a freezer.

Investigations from the 90's discovered the real correlations, as to why coffee goes “stale”. Methanethiol is known to give fresh coffee the “sense” of aroma freshness (Steinhart and Holscher, 1991). Storage at ambient temperatures causes a volatilisation of this component and other low boiling compounds, mostly sulfurous; the more heavy compounds like furfurylmercaptan, will remain in the coffee and will cause an “aging” note. Furthermore, changes will be enhanced by oxidation of the light volatile mercaptans to disulfides in the presence of oxygen (Fig. 13).

An increase of dimethylsulfide, the oxidation product of methanethiol, was observed. True “staling” compounds were not found. Only after a longer time an increase of hexanal, a degradation product of linoleic acid, may be found. It is interesting to note here that ELDER and SHUMAN already in the 40's had made similar experiences (Shuman and Elder, 1940); they had more time for real observations, which we are missing today.

The staling of a coffee brew is described in a recently published patent (Bradbury *et al.*, 1998). The generation of a bitter, sour taste in a coffee brew after standing for

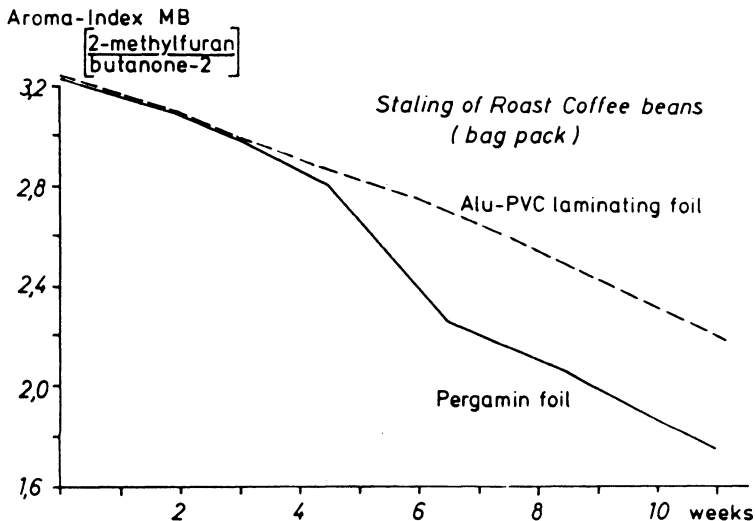


Figure 12. Influence of temperature on staling of ground coffee in packages and cans in presence of air (Vitzthum and Werkhoff, 1978).

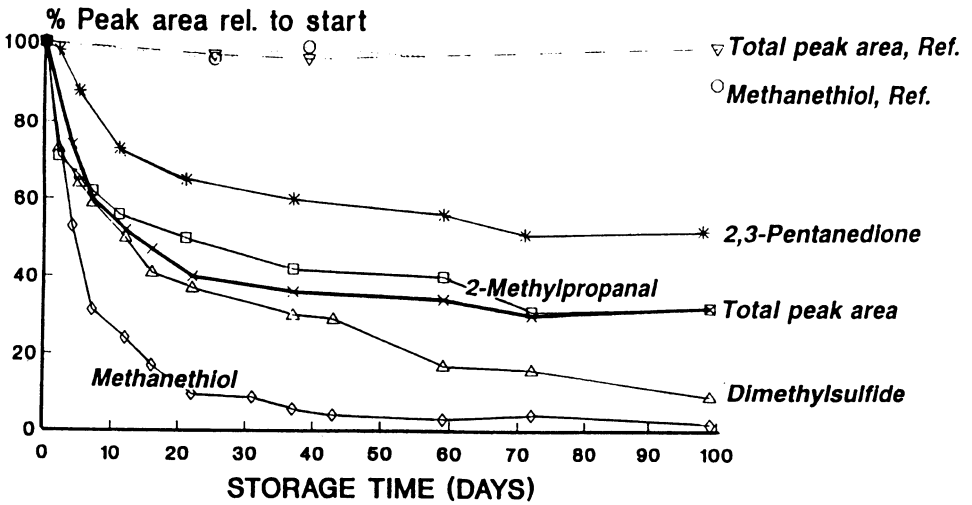


Figure 13. Kinetics of selected low-boiling odorants from roast coffee during storage.

some hours on a hot plate, is caused by the hydrolysis of chlorogenic acid lactones—formed during roasting—into quinic acid and caffeic acid (Fig. 14).

Quinic acid lactones also will be hydrolyzed; these acids contribute significantly to the undesirable acidity increase in a coffee brew after one or more hours.

Here I shortly should comment on “Espresso coffee”, which in optimal quality is

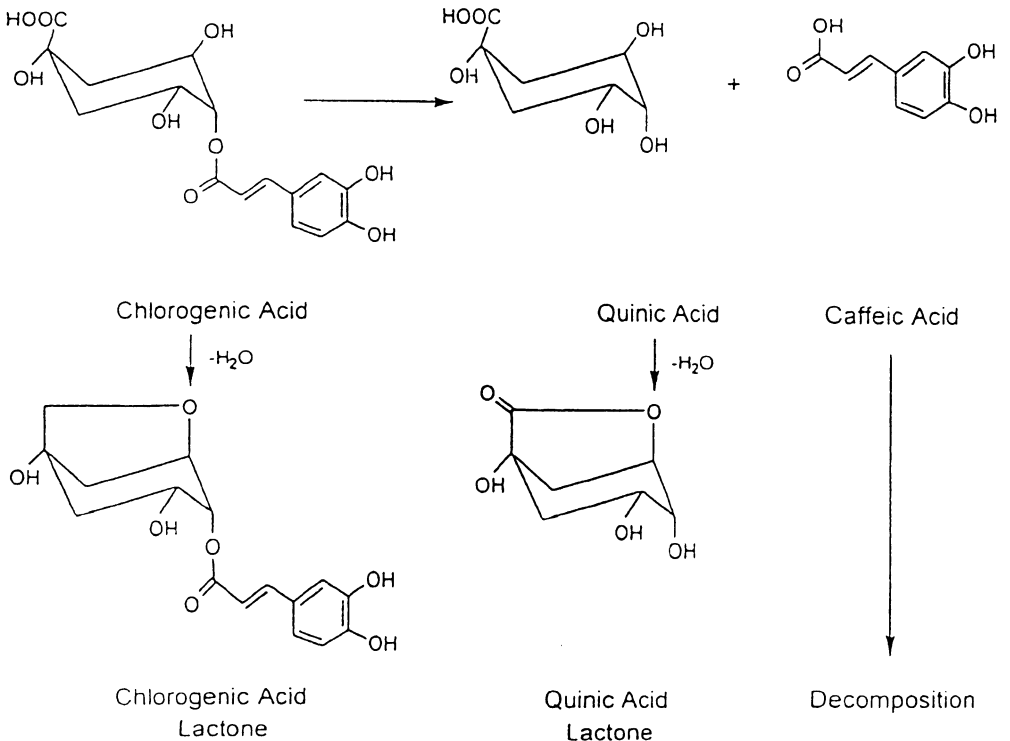


Figure 14. Formation of sour taste in the coffee brew after some time by hydrolysis of lactones.

produced in Italy; Espresso is drunk in much higher concentrations than ordinary brews, the product is dark roasted and requires top quality coffees for best flavor; extraction is carried out 30 seconds under pressure. A special electronic bean selection process in the coffee plant guarantees the absence of off flavors. Of course only Arabica coffees should be used (Illy and Viani, 1995).

3. FUTURE

New developments for the future will be electronic or even bioelectronic noses (in about 5 years from now) in Quality Control.

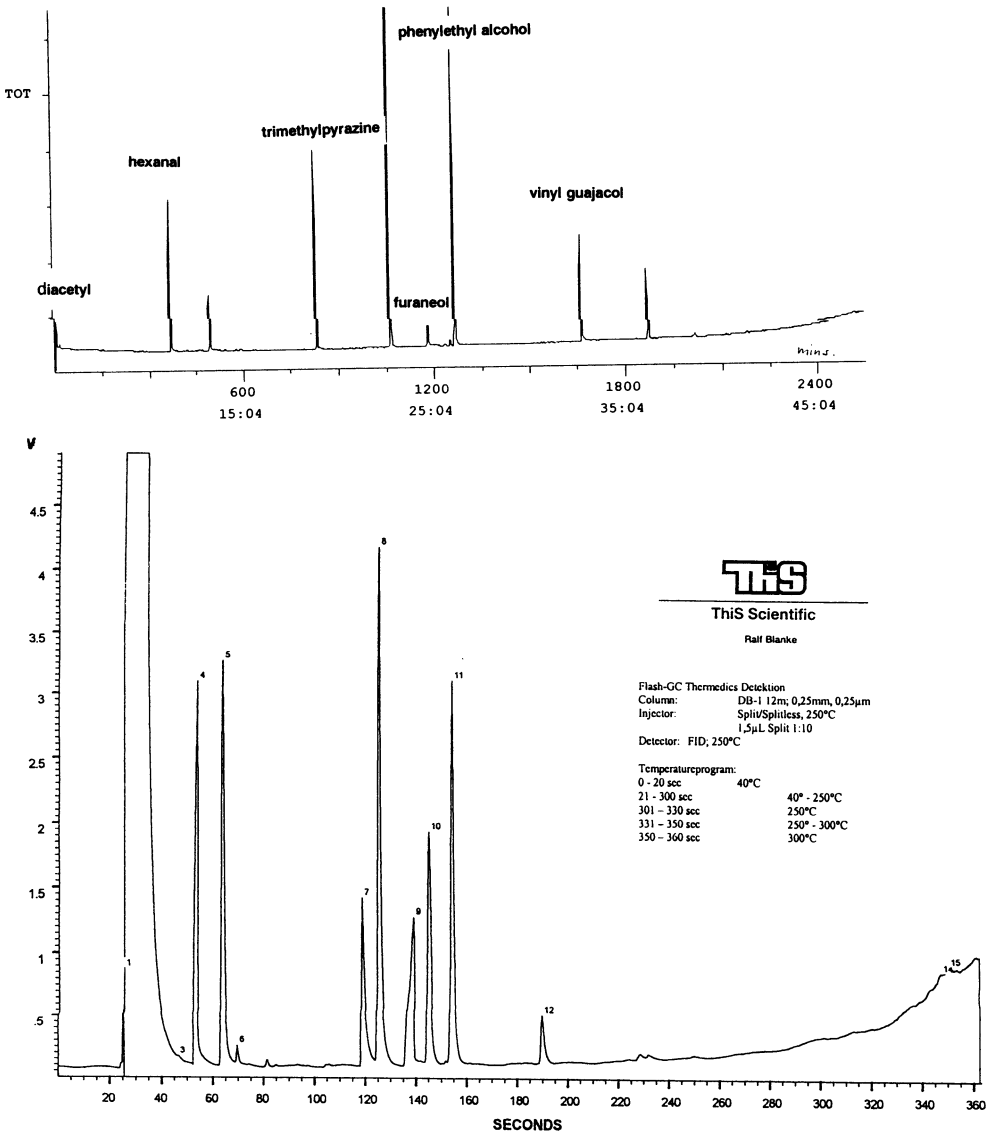


Figure 15. Coffee aroma model substances separated by conventional and hi-speed gas chromatography.

“Star” profile diagrams comparing sensory and chemical data of key aroma compounds one day will improve the possibilities of objective characterisation of different coffee origins and types.

A decrease of QC analyses time further will be expected from recently introduced hi-speed GC. A preliminary gc run is presented in Fig. 15 comparing the separation of coffee aroma compounds by conventional and hispeed GC.

ACKNOWLEDGMENTS

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