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Investigation of roasted coffee freshness with an improved headspace technique

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Untersuchung der Röstkaffee-Aromafrische mittels einer verbesserten Headspace-Methodik

Zusammenfassung. Die Zusammensetzung des angenehmen Aromas, das von frisch gerösteten Kaffeebohnen ausgeht, wurde mit einer Headspace-Methodik unter Einschaltung eines Cryofocussierungsschrittes sowie paralleler Schnüffelanalyse untersucht. Kinetische Studien mit ganzen Röstkaffeebohnen, die in nicht luftdichter Verpackung gelagert wurden, ergaben, daß die lagerungsbedingte Abnahme der Aromafrische mit dem Verlust bestimmter leichtflüchtiger Verbindungen insbesondere Methanthiol korreliert. Zur Validierung der Methode wurde der Einfluß verschiedener Parameter z. B. Mahlgrad, Röstgrad oder Provenienz, untersucht. Die Ergebnisse legen nahe, daß die entwickelte Methodik zur objektiven Beurteilung der Aromafrische ganzer Röstkaffeebohnen eingesetzt werden kann und zwar in weiten Bereichen ohne spezielle Kenntnis der Kaffee-Herkunft, des Röstgrades sowie anderer Einflußgrößen. Darüber hinaus ist eine analytisch-chemische Differenzierung zwischen *Arabica* und *Robusta*-Einzelprovenienzen möglich.

Summary. The volatiles forming the pleasant odour arising from freshly roasted coffee beans were investigated by means of an improved headspace technique with intermediate cryo-focusing and simultaneous sniffing analysis. Shelf-life tests were carried out with whole beans in non-air tight packs and indicated that the loss of aroma freshness several days to weeks after roasting corresponded to the decrease in certain low boiling volatiles, mainly methanethiol. To validate the method, several starting parameters were investigated, specifically the influence of particle size, degree of roasting and coffee bean origin. Results reveal that this headspace technique allows an objective evaluation of the aroma freshness of whole coffee beans without exact knowledge of coffee origin, degree of roasting or starting values. In addition the method differentiates between Arabica and Robusta coffees.

1 Introduction

The freshness of roasted coffee has long been an indicator of quality. Laymen as well as experts know aroma freshness of roasted coffee as the fine and pleasant smell arising from a freshly opened ground coffee pack or released during grinding of freshly roasted coffee beans. Storage-related loss of coffee freshness, generally called staling, have been of superior interest for industry as well as for consumers. The relationship between the influence of temperature, moisture, sunlight and especially oxygen (O_2) to staling of roasted coffee is well known. Packaging technology has taken these experiences into account, preferring an O_2-excluding vacuum pack for distribution of roasted and ground coffee. On the other hand, the market shares of coffee sold as whole beans are substantial, particularly in the middle of Europe. These whole beans are sold in non-air-tight packs designed only for short distribution periods. Non-air-tight packaging allows the unlimited influence of O_2 and moisture on the freshness quality of coffee.

In the past evaluation of aroma freshness has been predominantly a field for more or less trained coffee testers. Nevertheless, their judgement has to be considered subjective. Consistently coffee chemists have been looking for an objective analytical approach to determine the freshness of roasted coffee beans for a long time. For this purpose headspace techniques have been applied widely because of their simple handling and good reproducibilty [1–3]. Recently staling of coffee could be correlated with the generation of *n*-hexanal after an initiation phase of approximately 7 weeks storage in air [4, 5]. On the other hand, hexanal formation cannot explain the staling of roasted coffee completely, because a certain loss of odour intensity is already perceptible after 8–10

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days and a significant loss of cup quality is noticeable after 3 weeks of storage in air [6–8]. The major objective of this work was to characterise the volatiles contributing to the aroma freshness of roasted coffee beans and to develop an analytical method for its objective evaluation immediately after roasting and on the shelf. To validate the analytical procedure, the influence of sample preparation, coffee origin and degree of roasting was investigated.

2 Materials and methods

2.1 Sample material and storage. Green coffee samples were roasted to a medium degree (Probat laboratory roaster), if not noted otherwise. Controlled storage tests were carried out mainly with Colombian coffee. Each 500 g was stored in covered glass vials at 20° C under light protection, but without any O_2 protection. Reference samples were stored under N_2 at −40° C.

2.2 Sample preparation. Whole coffee beans were frozen to −20° C and ground to standard particle sizes (average 300–500 µm). Ground coffee (15 g) was transferred into a 100-ml sample vial together with ten small glass balls. In the case of samples taken from long-term shelf-life tests, 50 µl of an internal standard mixture (approx 500 mg tetrahydrofuran in 100 ml distilled water) was added for the correction of oscillating detector response. The vial was tightly closed and lightly shaken for 2 h under ambient conditions (20° C). Thereafter 500 µl from the headspace was taken from the vial by means of a gas-tight syringe and injected for gaschromatographic separation.

2.3 Gas chromatography (GC). Gas chromatographic separations were performed on a Carlo Erba 4120 gas chromatograph (Frankfurt, FRG) equipped with a purge and trap-system (Chrompack, Mainz-Kastel, FRG) which was modified to a static headspace-injector (Fig. 1). During the first step the cryotrap (I), consisting of a capillary column (CP-Sil-8 CB, 100 × 0.32 mm; 1.2 µm film thickness, Chrompack), was cooled to −120° C with liquid nitrogen (II). Thereafter, cooling was continued and a three-way valve (III) opened automatically thus accelerating the carrier gas flow from 2–3 ml/min to 10 ml/min for 2 min. Simultaneously the upper part of the injector (IV) was heated to 110° C to prevent condensation of volatiles. Afterwards the headspace sample volume was injected slowly (500 µl/30 s). In this manner, the volatiles were cryo-focused in the cryo-trap whereas the accelerated purge-gas stream was vented by the three-way valve (III). After 2 min the valve was closed to reduce the carrier gas flow to the regular level. Injection of the trapped volatiles was achieved by resistance-heating of the trap to 180° C within a few seconds. Generally gas chromatographic separations were performed on a DB-5 capillary column (60 m × 0.32 mm; 1 µm film thickness). The temperature programme was 20° C for 10 min, then 10° C/min to 160° C, held for 2 min using helium as carrier gas to a flow rate of 2–3 ml/min. Only for identification of volatiles via retention data was a DB-Wax capillary column (60 m × 0.32 mm, 0,25 µm-film thickness) used alternatively. Gas chromatograms were recorded on Spectraphysics 4270 integrators either as absolute peak areas (PA) or calculated as percentages relative to the total peak area (% PA).

2.4 GC/sniffing. GC-effluent sniffing was carried out by splitting the capillary column (DB-5, 30 m × 0.32 mm, 1 µm film thickness) in a stream for flame ionisation detection as well as for sensory evaluation by means of a sniffing port [10]. The temperature programme was 15° C for 6 min, then 10° C/min to 160° C. Aroma dilution analysis (ADA) [11] of aroma freshness was conducted in a modified manner. The gas volumes listed in Table 1 were taken from a sample vial containing freshly roasted Colombian coffee (see 2.2.) and injected for GC/sniffing successively by means of a gas-tight syringe. The odour impressions perceivable at the sniffing port were noted for each sample volume. All samples were evaluated by five trained testers. Retention data were plotted vs their corresponding flavour dilution (FD) factors (see Table 1) as an aromagram.

Table 1. Injected headspace volumes and corresponding flavour-dilution (FD) factors of aroma dilution analysis

Headspace volume [µl]	250	200	150	100	50	10
FD factor	1.00	1.25	1.66	2.5	5.00	25.00

2.5 Identification of volatiles. This was achieved by comparison of retention data on DB-5 and DB-Wax (see 2.3) and mass spectral data as well as sensory properties with those of authentic reference substances. For GC-MS GC equipment was connected to an ion trap detector (ITD 800-Finnigan MAT, Bremen, FRG). Mass spectra were generated at 70 eV in the electron impact mode.

2.6 Evaluation of equilibrium time and reproducibility. Three roasted coffee samples were prepared as described in 2.2 but using different equilibrium times, namely 1, 2 and 3 h, respectively. Reproducibility of the method described in 2.2 was checked by analysing the same lot of whole roasted beans five times.

2.7 Influence of particle size, degree of roasting and coffee origin. Two series of roasted coffee (each $n = 5$) with different particle size were compared with respect to the peak area of methanethiol obtained during headspace analysis. The average particle size was measured according to [12].

In order to study the influence of the degree of roasting, six and five samples of an *Arabica* (Colombia) and a *Robusta* coffee (Indonesia), respectively, were roasted in a range beginning with a very light roast (not yet drinkable) to an Espresso-like roast. Roast colour was measured by a reflectometric method (Agtron M30, San José, USA) on a scale from 0 to 25 by definition.

The influence of coffee origin was studied with a wide variety of single strains from Colombia, Burundi, Mexico, Ethiopia, Kenya, Costa Rica, Tanzania, El Salvador, Brazil, Guatemala and New Guinea, representing the *Arabicas* (Ara; $n = 21$) as well as with samples from Ivory coast, Uganda, Central Africa, Zaire, Vietnam, Indonesia and Madagascar, representing the *Robusta* type (Rob; $n = 9$). Additionally, one *Arabusta* sample (the Cameroons) was investigated. All green coffee samples were roasted to a medium degree and analysed according to 2.2, immediately after roasting and again after 10 days of storage in covered glass vials in air at 20° C under light-protection. Data handling was conducted as described in 2.8.

2.8 Computerised data evaluation. The values of % PA (see 2.3) of 13 baseline separated peaks (listed in Table 2) of the headspace-profile were calculated for each sample and were submitted to computer-aided discriminant analysis [13, 14] in order to maximise the differentiations between certain classes. The results were plotted in a coordinate system (centre set to zero by definition) where each sample was localised by their canonical variables. The canonical variable 1 corresponds approximately to the botanical variety whereas the canonical variable 2 refers to the aroma freshness.

3 Results and discussion

As first changes in aroma freshness are related to the loss of light volatiles, a static headspace technique was chosen, combining the advantages of large sample volumes and high separation efficiency. In order to analyse the aroma arising from a ground coffee, as it can be smelled by the human nose and to avoide artifact formation,

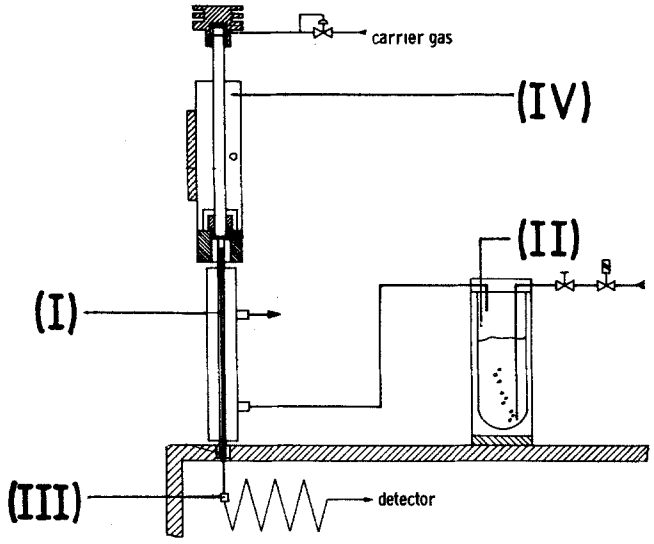

Fig. 1. Injection of headspace samples via intermediate cryo-focusing, according to [9]: (*I*) cryo-trap; (*II*) liquid nitrogen; (*III*) three-way valve; (*IV*) injector heating

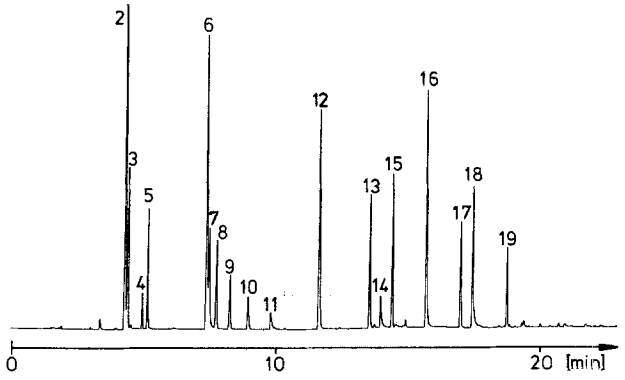

Fig. 2. Typical headspace profile on a DB-5 capillary column (*numbers* refer to Table 2; for GC-conditions see 2.3)

headspace gas of the coffee samples was injected after equilibration under ambient conditions. As shown in Fig. 1, the headspace samples were introduced into the GC system by means of automatic cryofocusing. In this way, considerably larger gas volumes can be injected even on a medium-bore capillary column without band broadening. Principally, it is possible to apply much larger sample volumes by extending the purge time. As the purge flow was mainly diverted by a three-way valve, the negative influence of O_2 on the capillary column could be minimised. Baseline noise, as recognised by other authors [15], is avoided. Connection of the capillary column to a sniffing port made possible simultaneous flame ionisation detection as well as sensory evaluation by the human nose, thus helping to optimise the analytical procedure. The use of a non-polar thick film capillary column allowed the separation of nearly all components of sensory interest and was advantageous with respect to column longevity. Figure 2 shows a typical headspace profile obtained under these conditions. For application of this headspace technique to long-term shelf-life tests and in order to take into account an oscillating detector response, the addition of an internal standard is recommended. Provided that all samples had the same particle size and the same degree of roasting, fairly reproducible PA were obtained for the internal standard peak, al-

Table 2. Chemical composition of the headspace aroma of freshly roasted coffee

No.	Component	Odour description/ sniffing port	Identification via
1	Hydrogensulphide	Putrid	RI, SP
2	Methanol[a,b]	–	MS, RI
3	Acetaldehyde[a,b]	Pungent, fruity	MS, RI, SP
4	Methanethiol[a,c]	Putrid, sulphurous	MS, RI, SP
5	Methylformate[a,c]	–	MS, RI
6	Acetone[a]	–	MS, RI
7	Propanal[a]	–	MS, RI
8	Furan[a,c]	–	MS, RI
9	Isoprene[a,c]	–	MS, RI
10	Dimethylsulphide[a,c]	Weak coffee-like, sulphurous	MS, RI, SP
11	Methylacetate[a,c]	–	MS, RI
12	2-Methylpropanal[a,c]	Pungent, fruity, malty	MS, RI, SP
13	2,3-Butanedione[a,c]	Buttery	MS, RI, SP
14	2-Butanone[a,c]	–	MS, RI
15	2-Methylfuran[a,c]	–	MS, RI
16	Tetrahydrofuran[a]	(Internal standard)	–
17	3-Methylbutanal[a,c]	Sweaty, pungent, fruity	MS, RI, SP
18	2-Methylbutanal[a,c]	Fermentated, pungent, fruity	MS, RI, SP
19	2,3-Pentanedione[a,c]	Buttery	MS, RI, SP
20	3-Methyl-2-buten-1-thiol	Foxy, skunky	RI, SP
21	n.i.	Sweaty, catty	–
22	Methional	Cooked potato-like	RI, SP
23	2-Furanmethanethiol	Roasty, weak coffee-like	RI, SP
24	n.i.	Caramel-like	–
25	n.i.	Tallowy, leather-like	–
26	n.i.	Roasty, peanut-like	–

n.i., not identified; MS, mass spectral data; RI, retention data; SP, sensory properties; [a] Peak in Fig. 2; [b] Coelution with butene isomer; [c] Peak chosen for canonical discriminant analysis (see 2.8)

though standard addition to other kinds of solid samples often caused problems due to an insufficient dispersion.

The results of chemical characterisation are summarized in Table 2. Major progress was achieved when GC/sniffing was applied, because ADA allowed differentiation between sensorily important, less or unimportant peaks and enable estimation of the contribution of single volatiles to the overall perceptible aroma freshness. The largest sample volume applied (250 µl) gave about 16 aroma notes. The number of aroma notes is therefore low compared to the GC/sniffing analysis of a total aroma extract obtained by steam distillation, when over 60 odour notes were detectable [16]. Consecutively, the sensory impression released from a freshly roasted coffee under ambient conditions, commonly called aroma freshness, only consists of a certain fraction of the total aroma content, namely low-boiling and aroma-potent sulphur compounds, Strecker-aldehydes and α-dicarbonyls. By reducing the sample volume in each GC run, more and more aroma notes disappeared. At the end of the ADA (10 µl injection volume) only the most intense ones were still recognisable. The aromagram in Fig. 3 makes plain the contribution of certain components to the aroma freshness of roasted coffee. Methanethiol (4) and 2-methylpropanal (12) gave the most intense aroma notes (FD factors = 25). Furthermore 2,3-butanedione and 2,3-pentanedione gave strong buttery notes besides the slightly weaker notes of the methylbutanal isomers. Several lower volatile trace components e.g. 2-furanmethanethiol and 3-methyl-2-buten-1-thiol, recently identified in roasted coffee [16, 17], contributed to the pleasant odour of freshly roasted coffee as well but gave no detector response.

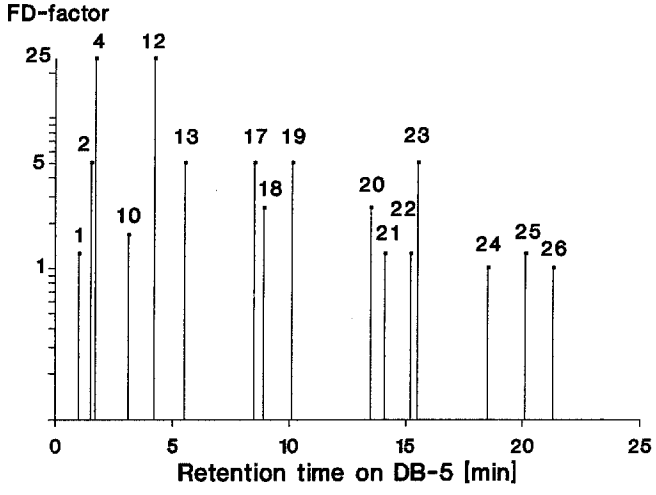

Fig. 3. Aromagram of the aroma freshness of roasted coffee (*numbers* refer to Table 2; FD, *f*lavour *d*ilution, see text)

Figure 4 shows that the total headspace volatiles still increased after 3 h shaking, whereas the maximum PA of methanethiol was reached after 2 h. Shaking for 2 h is therefore a compromise between optimal equilibration and time consumption. The reproducibility of the method was checked by calculating the coefficients of variation. They were in a range of 1.8% (3-methylbutanal) to 5.1% (dimethylsulphide) and were therefore acceptable with respect to headspace techniques.

Table 3 shows that two series with ground coffee of different particle size differed with respect to the % PA

Table 3. Influence of particle size on the results of the percentage of the peak areas (% PA) of methanethiol (see 2.3)

Series		% PA methanethiol			*p*	Average particle size (µm)
		x	±	*s*		
A	$n=5$	1.15	±	0.064	0.99	517
B	$n=5$	1.52	±	0.080	0.99	297

x, mean; *s*, standard deviation; *p*, probability

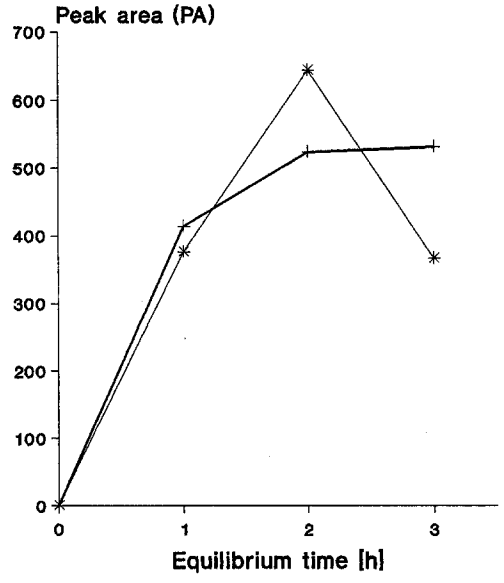

Fig. 4. Total peak area (+) and peak area of methanethiol (*) depending on the equilibrium time

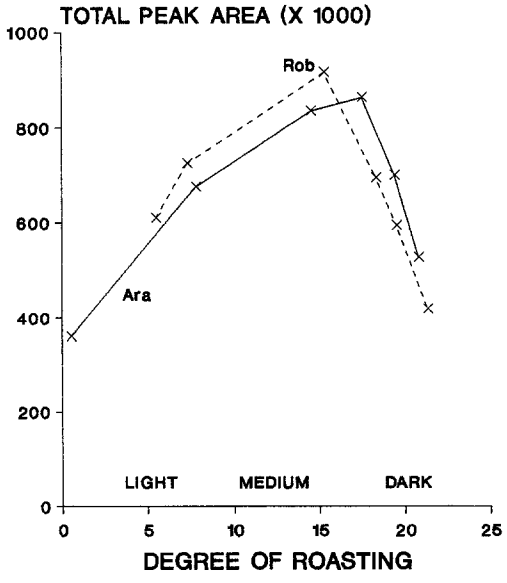

Fig. 5. Relationship between total headspace volatiles and degree of roasting in *Arabica* (*Ara*, ×—×) and *Robusta* (*Rob*, ×———×) coffee

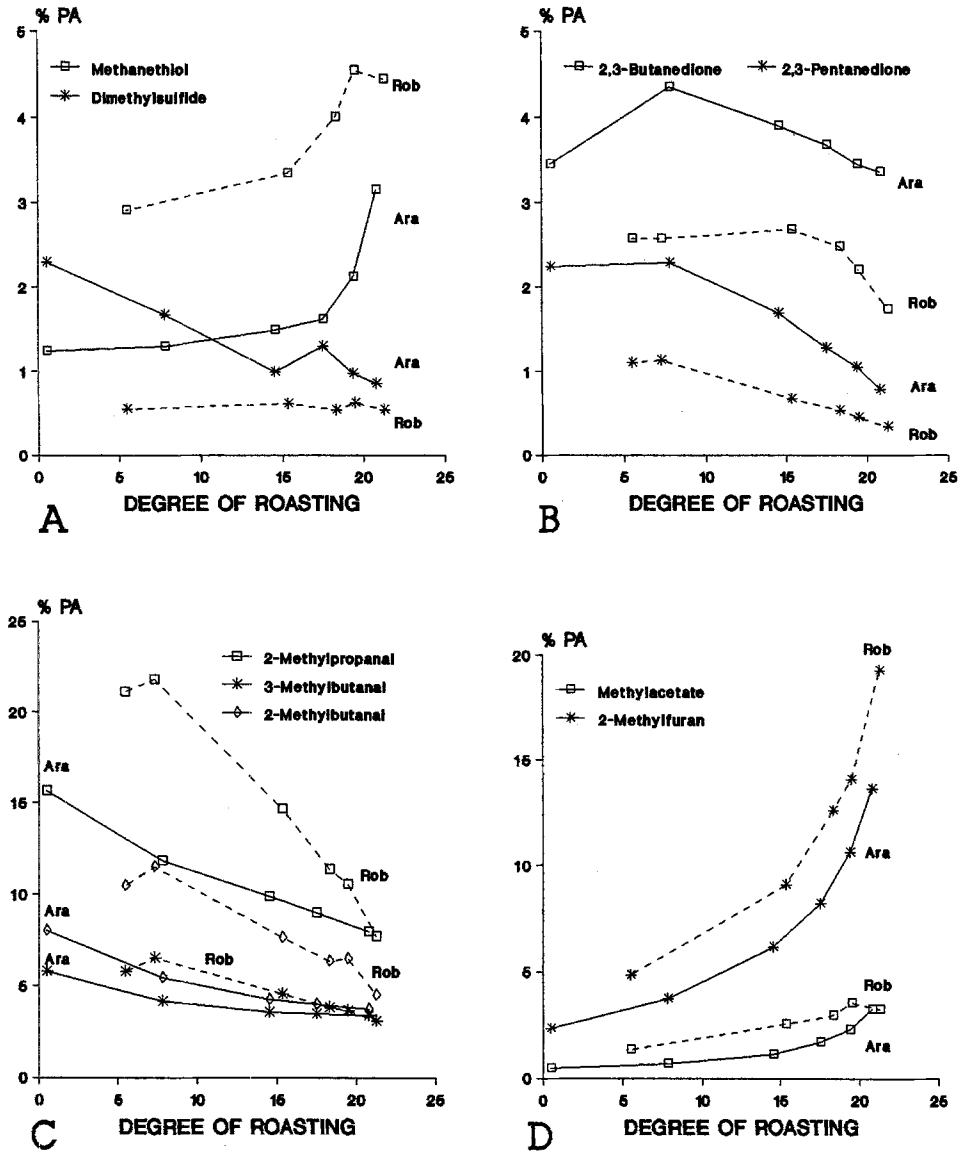

Fig. 6 A–D. Changes in the headspace composition of freshly roasted *Arabica* (*Ara*) and *Robusta* (*Rob*) coffee-depending on the degree of roasting (% PA = percentages of the peak area of a headspace component relative to the total peak area)

of methanethiol (see 2.3) which was significantly higher in series B. In practice, standardisation of grinding will overcome this problem very easily. Roasting affects the total headspace volatiles in a characteristic manner and causes an increase in volatiles during roasting with a maximum at medium degrees of roasting (Fig. 5). The total PA decreases, however, with ongoing roasting. The *Robusta* samples (Rob) showed higher amounts of light volatiles at a medium degree of roasting compared to the respective *Arabica* coffee (Ara).

Figures 6A–D show the kinetics of some selected headspace components during roasting in an *Arabica* as well as in a *Robusta* sample. In order to obtain more comparable results and to avoid the influence of inconsistent injection volumes of oscillating detector response, the % PA values (see 2.3) were calculated for each compound. Twofold higher amounts of methanethiol were formed in the Indonesian *Robusta* compared to the *Arabica*. Methanethiol increases strongly with darker roast. Dimethylsulphide remained about the same (Rob) or decreased slightly (Ara). On the other hand, the kinetics of the aroma-potent α-dicarbonyls, 2,3-butanedione and 2,3-pentanedione, were completely different (Fig. 6B). Their maximum was already reached under slight roasting conditions. The relative amounts decreased with further thermal treatment, accompanied by an aroma shifting from mild buttery notes to more burnt or sulphurous aroma notes. Total amounts of α-dicarbonyls are about twofold higher in *Arabicas*. Figure 6C shows the curves for some aroma-intense Strecker-aldehydes. Their formation in early steps of roasting is obvious. With further thermal treatment their portions decrease. The curves of methylacetate or particularly 2-methylfuran (Fig. 6D) show a significant increase during roasting for the *Arabica* as well as for the *Robusta* sample.

The optimised headspace technique was applied for kinetic studies of single volatiles during shelf-life tests. The major results for some aroma potent volatiles are shown in Fig. 7A and B. For each component, residual percentages relative to the start were calculated. It is obvious that the biggest changes in low-boiling volatiles occurred within 3 weeks. The total headspace volatiles, re-

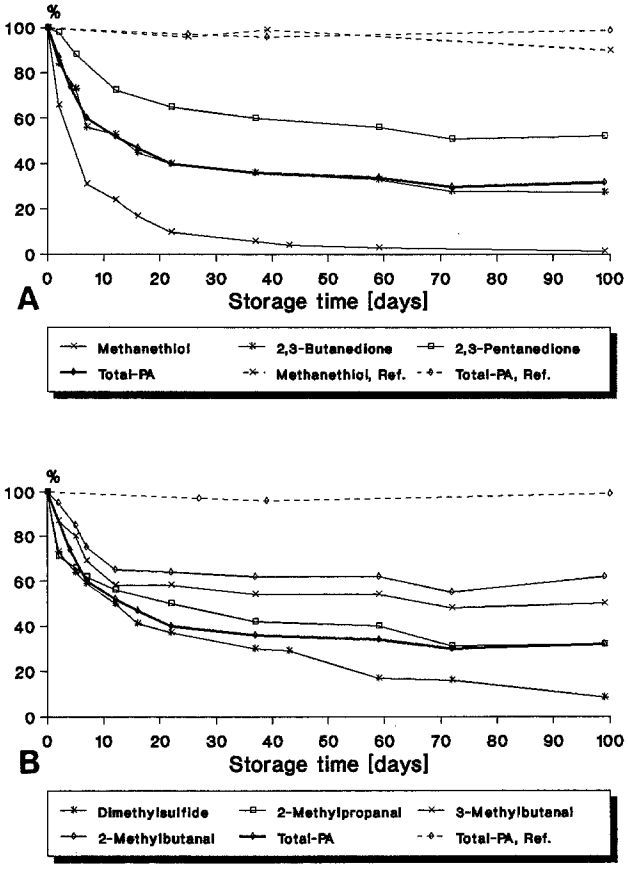

Fig. 7 A, B. Kinetics of low-boiling odorants contributing to the aroma freshness of roasted coffee during storage in non-air-tight packs (peak areas are given as % relative to the starting values; Ref. = reference sample)

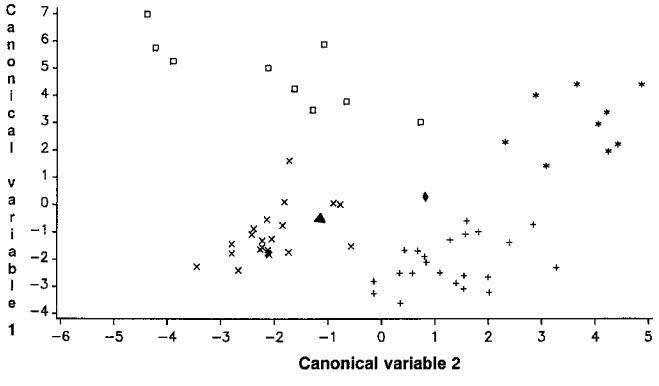

Fig. 8. Canonical discriminant analysis: discrimination of roasted coffee beans with respect to botanical variety and freshness based on headspace profile analysis: (x) *Arabica*/freshly roasted; (+) *Arabica*/10 days old; (□) *Robusta*/freshly roasted; (*) *Robusta*/10 days old; (▲) *Arabusta*/freshly roasted; (♦) *Arabusta*/10 days old

corded as total PA, decreased to less than half of the starting value. Nearly the same change was obtained for the aroma-intense 2-methylpropanal, whereas 3-methylbutanal and 2,3-pentanedione apparently showed a lower decrease than the average. On the other hand, a larger decrease was measured for dimethylsulphide. This may be due to the fact that sulphur-containing compounds are known to be much more O_2-sensitive. One of the most important findings was the kinetics of methanethiol. This compound having a strong impact on aroma freshness showed the largest decrease, which was already recognisable 1 day after roasting. After 8 days of storage, the PA of methanethiol decreased to a level of about 30% and further to 10–20% relative to the starting value after 3 weeks of storage. The dotted lines show the values for the PA of methanethiol and the total PA of the preserved reference samples (Ref.) with nearly remained unchanged during the time period of hundred days.

Finally, Fig. 8 shows the influence of coffee origin on the results of this type of headspace analysis in the freshly roasted state as well as after 10 days of storage in air. Despite of the fact that only 13 peaks from the headspace profile were taken into account, the computer-aided canonical discriminant analysis allowed an exact differentiation between four distinctive classes: Arabica/freshly roasted and Arabica/10 days old, as well as Robusta/freshly roasted and Robusta/10 days old. The Arabusta sample was attached to the Arabicas. It must be pointed out that the % PA value of methanethiol had the biggest influence on the discriminant analysis both on coffee origin and on age (see also Figs. 6 A and 7 A). For the evaluation of roasted coffee aroma freshness, the applied headspace technique is a further tool for an aroma specific differentiation between Arabica and Robusta coffees.

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