2. Chemical Composition

2.1 General aspects

Roasted, ground and decaffeinated coffee, in their dry form, consist of a soluble and an insoluble portion; the proportions of each in the beverage depends upon the brewing conditions and the appliance used. While it is possible by exhaustive extraction in the laboratory to obtain 30-32% w/w soluble substances from roasted coffee, the more usual yield in household brews is 15-25% w/w. As mentioned above, the ratio of weight of dry product to volume of water used for brewing also varies according to national and local tastes; variations also occur in

Table 13. Coffee consumption trends in the USA in people aged 10 years and over, 1957–89[a]

	Cups per person per day													Difference 1962–89	Change (%)
	1957	1962	1967	1972	1977	1982	1983	1984	1985	1986	1987	1988	1989		
Type															
Brewed	2.32	2.45	2.19	1.67	1.30	1.33	1.31	1.44	1.39	1.37	1.37	1.31	1.43	-1.02	-42
Instant	0.50	0.67	0.65	0.68	0.64	0.56	0.53	0.54	0.42	0.36	0.37	0.34	0.32	-0.35	-52
Decaffeinated	NA	0.10	0.16	0.17	0.27	0.38	0.39	0.44	0.42	0.41	0.43	0.38	0.40	+0.30	+200
All	2.82	3.12	2.84	2.35	1.94	1.90	1.87	1.99	1.83	1.74	1.76	1.67	1.75	-1.37	-44
Region															
North–east	2.72	2.91	2.63	2.10	1.79	1.85	1.90	1.90	1.84	1.86	1.75	1.58	1.79	-1.12	-38
North–central	2.99	3.34	3.18	2.66	2.34	2.18	2.06	2.27	2.04	1.92	1.90	1.96	1.98	-1.36	-41
South	2.48	2.78	2.39	1.97	1.99	1.68	1.66	1.84	1.57	1.53	1.58	1.45	1.52	-1.26	-45
West	3.25	3.52	3.19	2.74	1.98	1.96	1.86	2.00	2.01	1.70	1.91	1.77	1.81	-1.71	-49
All	2.82	3.12	2.84	2.35	1.94	1.90	1.87	1.99	1.83	1.74	1.76	1.67	1.75	-1.37	-44
Age group															
10–14	0.19	0.18	0.19	0.12	0.07	0.03	0.04	0.04	0.03	0.02	0.03	0.04	0.02	-0.16	-89
15–19	1.11	1.09	0.82	0.55	0.45	0.33	0.26	0.30	0.21	0.16	0.19	0.23	0.20	-0.89	-82
20–24	2.60	2.99	2.22	1.48	1.36	0.92	0.88	0.92	1.00	0.79	0.55	0.63	0.72	-2.27	-76
25–29	3.65	3.88	3.21	2.47	1.89	1.75	1.60	1.64	1.48	1.32	1.39	1.22	1.23	-2.65	-68
30–39	3.67	4.50	3.99	3.51	2.62	2.37	2.39	2.42	2.24	2.11	2.19	1.91	2.03	-2.47	-55
40–49	3.74	4.44	4.48	3.72	3.49	3.11	2.85	3.15	3.02	2.62	2.75	2.57	2.57	-1.79	-40
50–59	3.16	3.83	3.70	3.35	3.22	3.09	3.27	3.33	2.93	2.77	2.95	2.85	2.97	-0.86	-22
60–69	2.75	3.01	3.16	2.85	2.72	2.65	2.49	2.87	2.51	2.70	2.49	2.49	2.64	-0.37	-12
≥70	2.29	2.39	2.50	2.49	2.00	2.03	1.95	2.18	1.87	2.04	1.85	1.83	1.93	-0.46	-19
Sex															
Male	2.91	3.28	2.93	2.48	2.12	2.06	1.90	2.10	1.91	1.80	1.89	1.86	1.85	-1.43	-44
Female	2.73	2.98	2.77	2.23	1.95	1.75	1.81	1.89	1.76	1.68	1.64	1.50	1.66	-1.32	-44

Table 13 (contd)

	Cups per person per day													Difference 1962–89	Change (%)
	1957	1962	1967	1972	1977	1982	1983	1984	1985	1986	1987	1988	1989		
Location															
Home	2.35	2.57	2.29	1.86	1.62	1.36	1.37	1.40	1.29	1.24	1.23	1.19	1.23	-1.34	-52
Work	0.21	0.26	0.30	0.28	0.16	0.38	0.33	0.38	0.35	0.31	0.33	0.32	0.34	+0.08	+131
Eating places	0.26	0.29	0.25	0.21	0.25	0.14	0.13	0.17	0.14	0.14	0.14	0.12	0.18	-0.11	-38
Time of day															
Breakfast	1.14	1.17	1.13	1.00	0.91	0.88	0.89	0.92	0.88	0.84	0.85	0.83	0.90	-0.27	-23
Other meals	0.96	0.98	0.77	0.59	0.46	0.36	0.36	0.35	0.30	0.27	0.30	0.25	0.22	-0.76	-78
Between meals	0.72	0.97	0.94	0.76	0.66	0.66	0.62	0.71	0.65	0.65	0.61	0.59	0.63	-0.34	-35
% of US population drinking coffee	77.3	74.7	71.4	65.0	57.9	56.3	55.2	57.3	54.9	52.4	52.0	50.0	52.5	-22.2	-30
Cups per drinker per day	3.65	4.17	3.98	3.62	3.51	3.38	3.36	3.48	3.33	3.32	3.38	3.34	3.34	-0.83	-20

[a] From Gilbert (1984); International Coffee Organization (1989f,h)
NA, not available

Table 14. Consumption of decaffeinated coffee in the USA in 1985–88 and in 1962[a]

Year	% of US population drinking coffee	No. of cups per day	
		per person	per drinker
1962	4.0	0.10	2.61
1985	17.3	0.42	2.42
1986	17.1	0.41	2.37
1987	17.5	0.43	2.48
1988	15.8	0.38	2.40
% change:			
1962–88	+11.8	+0.28	–0.21
1985–88	–1.5	–0.04	–0.02

[a] Adapted from International Coffee Organization (1989h)

the nature and origin of the coffee, the appliance and the amount of additives (e.g., milk) used subsequently. All of these factors influence the concentration of soluble substances in the resultant brews and their chemical compositions. Generally, 42, 48 and 57 g roasted, ground coffee are used typically per litre of water in the USA, UK and Europe, respectively, and some 150 ml of the water are retained in the spent coffee grounds.

Soluble substances have already been extracted from instant coffee at the point of manufacture. The percentage removed varies according to brand and may be up to 50%, so that more of the normally insoluble substances are rendered soluble at 100°C. About 12 g/l is a typically used average concentration of product in water for UK and US tastes; it is higher and lower in other countries. Clearly, the composition of different instant coffees varies considerably, especially in the relative proportions of the various constituents.

The main component of the beverages consumed is therefore water. Caffeine has particularly important stimulatory properties, but all three preparations contain other nonvolatile soluble compounds. Compounds of known physiological importance in roasted coffee and instant coffee have been reviewed by Viani (1988). Volatile compounds occur in the dry product, and their presence in the brews is again dependent on the amount and type of product and on the brewing conditions: 40-100% is extracted in practice (Pictet, 1987). The content of volatile substances in instant coffees is particularly dependent upon the sophistication of the method for extracting and retaining such substances on drying. The influence of nonvolatile and volatile components on the flavour of coffee has been described in detail (Clarke, 1986).

Tables 15 and 16 give a broad tabulation of all components of green and roasted arabica and robusta coffees (Clarke, 1987). It should be noted that considerable variation may occur, depending on factors such as the exact source and storage conditions, especially with regard to the concentrations of compounds that occur at low levels, such as aliphatic acids, reducing sugars and free amino acids. The values for polysaccharides, lignin and pectin are considered to be less reliable than others, as they are derived by indirect analysis from data on hydrolysis; however, they are indicative. For roasted coffee, further differences depend on the degree of roasting. Roasted coffee may also contain roasted seeds, tubers and other parts of vegetable plants, such as chicory. Instant coffee may similarly contain the soluble parts of these materials (Clarke & Macrae, 1987a).

Table 15. Composition of green coffee[a]

Component	Typical average content (dry basis, %)	
	Arabica	Robusta
Alkaloids (caffeine)	1.2	2.2
Trigonelline	1.0	0.7
Minerals (as oxide ash)		
41% potassium and 4% phosphorus	4.2	4.4
Acids		
Total chlorogenic	6.5	10.0
Aliphatic	1.0	1.0
Quinic	0.4	0.4
Sugars		
Sucrose	8.0	4.0
Reducing	0.1	0.4
Polysaccharides ('mannan', 'galactan', 'glucan' and 'araban')	45.0	50.0
Lignin	2.0	2.0
Pectins	3.0	3.0
Proteinaceous compounds		
Protein	11.0	11.0
Free amino acids	0.5	0.8
Lipids		
Coffee oil (triglyceride with unsaponifiable fat)	16.0	10.0

[a] From Clarke (1987)

Table 16. Composition of a medium-roasted coffee[a]

Component	Typical average content (dry basis, %)		% extractable with water at 100°C[b]
	Arabica	Robusta	
Alkaloids (caffeine)	1.3	2.4	75-100
Trigonelline (including roasted by-products)	1.0	0.7	85-100
Minerals (as oxide ash)	4.5	4.7	90
Acids			
Residual chlorogenic	2.5	3.8	100
Quinic	0.8	1.0	100
Aliphatic	1.6	1.6	100
Sugars			
Sucrose	0.0	0.0	-
Reducing	0.3	0.3	100
Polysaccharides (unchanged from green)	33	37	10
Lignin	2.0	2.0	0
Pectins	3.0	3.0	-
Proteinaceous compounds			
Protein	10	10	15-20
Free amino acids	0.0	0.0	-
Lipids (coffee oil)	17	11	1
Caramelized or condensation products (e.g., melanoidins) by difference	23	22.5	20-25
Volatile substances other than acids	0.1	0.1	40-80

[a] From Clarke (1987)
[b] From Maier (1981), for normal household brewing

A general and detailed description of all aspects of the chemistry of coffee has been published (Clarke & Macrae, 1985).

2.2 Compounds present in green, roasted, brewed, instant and decaffeinated coffees

The formulae of some of the compounds described below are given in Appendix 1 to this monograph (p. 199).

The quantitative data presented are generally for dry roasted coffee. To calculate representative values for the content in the beverage consumed, an average usage of 10 g roasted coffee per cup of filtered coffee (150 ml), equivalent to 57 g roasted coffee brewed with 1 l of water, can be assumed. Approximately 86% of the water is in the brew and the remainder left with the grounds. At an extraction yield of 20% total soluble solids, a concentration of 1.3% w/w would therefore be consumed. Assuming 100% extraction of particulate substances, their content in a cup can be estimated by dividing the content in roasted coffee (mg/kg) by 100.

With some filter devices and using finer grinds (as in the UK), smaller quantities of roasted coffee are used, e.g., 48 g/l of water or 8.3 g/cup. Spiller (1984b) assumed 7.5 g/150-ml cup from US experience; however, Clinton (1985) analysed data from 3000 respondents across the USA and found an average strength of 1.38 g coffee solubles per cup, equivalent to only 6.9 g roasted, ground coffee at 20% yield. Weaker coffee was drunk in the west than in the east.

Another form of expression is that 10 g per cup is equivalent to 100 cups/kg roasted, ground coffee, 8.3 g is equivalent to 122 cups/kg and 6.9 g to 147 cups/kg.

Table 16 gave an indication of the percentages of various components that are extracted. The level may be 75-100% for components such as caffeine and chlorogenic and other acids, but is rather less for volatile components.

(*a*) *Nonvolatile substances*

(i) *Caffeine and other purines*

Extensive determinations of caffeine in green coffees have been reported (Macrae, 1985). These indicate an average of 1.2% on a dry basis (commercial range, 0.9-1.4%) for arabica coffee and 2.2% (commercial range, 1.5-2.6%) for robusta coffee. (Analytical methods are reported in the monograph on caffeine.) The content in roasted coffee is usually somewhat higher than in the corresponding green — by up to 10% in darker roasts — due to physical loss in weight of other components; 0-5% of the caffeine is lost by sublimation. Few reliable direct determinations have been made on roasted coffee, but several have been done on brewed coffee (Table 17; Bunker & McWilliams, 1979; Clinton, 1985). Minute amounts of related alkaloids have been identified and quantified in roasted coffee, e.g., theobromine at 0.009-0.037% and theophylline at 0.00-0.013% (Kazi, 1985; Macrae, 1985); traces of paraxanthine, theacrine and liberine have been detected in unripe green coffees (Viani, 1988).

(ii) *Chlorogenic acids and related substances*

A number of different chlorogenic acids are present; the amount of each depends largely on the degree and type of roasting to which the green coffee has been subjected (Clifford, 1985). 5-Caffeoylquinic acid is present in the largest amounts, in both green and roasted coffees. Dicaffeoyl and feruloyl quinic acids are also present, together with the 3- and 4-isomers of monocaffeoylquinic acid. The total percentage of chlorogenic acids in eight commercial roasted coffee samples ranged from 0.2-3.5% (very dark to light roasting) (Trugo, 1984), and that in 19 samples was 1.6-3.8% (Maier, 1987a). On the basis of 10 g coffee per cup of brew and 85% recovery, this would indicate a level of 15-325 mg/cup (Viani, 1988). Actual data (Clinton, 1985) from the USA give an average value of 190 mg total chlorogenic acids per cup of brewed coffee. Pyrolysis products of chlorogenic acid, in particular quinic acid and caffeic acid (see p. 69), are also found, depending upon the origin and degree of roasting, as are phenols (see p. 76).

Table 17. Caffeine content per cup of brewed coffee

Reference and location	Type of brew	No. of samples	Cup size (ml)	Caffeine (mg/cup)	
				Average	Range
Estimated by the Working Group[a]	10 g/cup				
	Arabica	–	150 ml	–	102–120
	Robusta	–	150 ml	–	187–220
	7 g/cup				
	Arabica	–	150 ml	–	71–84
	Robusta	–	150 ml	–	131–154
Burg (1975)[b] USA	Percolated	2000	150 ml	83	64–124
Gilbert *et al.* (1976) Canada	Percolated	–	150 ml	74	39–168
	Drip	–	150 ml	112	56–176
Bunker & McWilliams (1979) USA	Percolated	–	150 ml	104	89–122
	Drip	–	150 ml	142	137–149
Lecos (1984) USA	Percolated	–	150 ml	80	40–170
	Drip	–	150 ml	115	60–180
Clinton (1985) USA	Percolated/Drip	3000	197 ml	85	–

[a] On the basis of 1.2% caffeine in roasted dry arabica and 2.2% in roasted dry robusta, and range given for 85% and 100% efficiencies of extraction of caffeine
[b] Cited by Roberts & Barone (1983)
–, not given

(iii) *Glycosides*

Atractyligenin (a nor-diterpenoid substance of the (-)-kaurane series) has been found in coffee, both as the free compound and as the aglycone of three glycosides (Mätzel & Maier, 1983). The content of atractyligenin has been estimated at 2.9-11.5 mg/cup of brewed arabica and 0-0.2 mg/cup of brewed robusta (Viani, 1988).

(iv) *Lipids*

Roasted coffee has a very high lipid content — approximately 16% w/w in arabica and 11% in robusta — associated with two diterpenes specific to coffee, kahweol and cafestol, mostly combined as glycerides. The total diterpene content is typically reported at 1.3% in green arabica (ratio of cafestol:kahweol, 40:60 to 70:30) and at only 0.2% in green robusta (predominately cafestol) (Viani, 1988).

There appears to be little destruction on roasting; but of greater importance is the fact that little of the oil (lipids) and of these terpenes occurs in brewed coffee, e.g., 0.9 mg lipid (coffee oil) per cup and 0.005 mg diterpenes in filter brews, with rather more in espresso brews (40 and 3.2 mg, respectively) (Viani, 1988).

Various sterols (and their esters with fatty acids) and tocopherols are also present in the lipids, but there is no evidence of their presence in brewed coffee. The presence of various alkanoylated 5-hydroxytryptamines (high C_n fatty acids plus 5-hydroxytryptamine) in the wax on the outer surface of green coffee beans has been examined extensively by Folstar (1985); they are present at 500-1000 ppm (mg/kg), but they are partly destroyed on roasting and very little passes into the brew (van der Stegen, 1979).

(v) *Trigonelline and nicotinic acid*

Trigonelline is present typically at 1.1% in dry arabica green coffee (range, 0.6-1.3) and 0.65% in dry robusta green coffee (range, 0.3-0.9) (Macrae, 1985). The amount destroyed during roasting depends on the degree of roast, e.g., an original 1.1% level will decline to around 0.2% in dark roasts (Trugo, 1984), corresponding to 110 and 20 mg/cup assuming 10 g of roasted coffed per cup. An average content of 53 mg/cup has been reported by Clinton (1985) in the USA. Trigonelline is transformed into several volatile products but also into nicotinic acid (niacin; vitamin PP), of which roasted and brewed coffee can be important sources (100-400 mg/kg) (Macrae, 1985). A content of 0.03-0.05 mg nicotinic acid per cup was reported from six samples (Viani, 1988); Macrae (1985) reported 1 mg/cup and 2-3 mg from a dark roast. Residual trigonelline has been reported at a level of 40-55 mg/cup (Viani, 1988).

(vi) *Acids*

The nature and amount of nonvolatile acids in roasted coffee has been examined extensively, since they can contribute significantly to its flavour (Woodman, 1985; Maier, 1987a; van der Stegen & van Duijn, 1987). Apart from residual chlorogenic acids, the main acids present in significant quantities are quinic, malic, citric, lactic, pyruvic, succinic and glycolic acids (Table 18).

The amount of each acid is strongly dependent upon the degree of roasting, sometimes peaking in medium roasts, such as citric acid in Kenya arabica with 'fine' acidity (van der Stegen & Duijn, 1987).

Table 18. Content of selected nonvolatile acids in roasted coffee

Acid	Content (%, dry weight)[a]					
	Arabica (during roasting)[b]		Arabica (4 samples)[c]	Robusta (4 samples)[c]	Commercial (17 samples)[d]	
	Tanzania	Kenya			Average	Range
Citric	0.87 to 0.55	0.70 to 0.18	[0.67]	[0.48]	0.59	0.43–0.70
Malic	0.39 to 0.24	0.30 to 0.19	[0.33]	[0.13]	0.27	0.10–0.39
Lactic	0.08 to 0.10	0.09 to 0.16	–	–	0.10	0.00–0.18
Pyruvic	0.17 to 0.14	0.09 to 0.09	–	–	–	–
Glycolic	–	–	[0.26]	[0.19]	0.26	0.17–0.49
Succinic	–	–	–	–	0.40	0.19–0.80
Quinic	–	0.56 to 0.87	[0.96]	[1.15]	1.04	0.89-1.50

[a] To convert to milligrams per kilogram, multiply by 10 000; to convert to milligrams per cup multiply by 100.

[b] From Blanc (1977); in samples roasted in the laboratory, with 9–20% loss (i.e., from very light to dark)

[c] From Maier (1987a); in samples roasted in the laboratory, with 17% loss for arabica and 19% for robusta (medium to dark roast); graphic data in millimoles per kilogram, converted by the Working Group

[d] From van der Stegen & van Duijn (1987)

Maier (1987a) also found phosphoric acid [estimated from a graph by the Working Group at 0.19%] in roasted arabica and [0.29%] in roasted robusta; he also found significant amounts of an unspecified high-molecular-weight acid. Other acids have been identified (Spiller, 1984b) but in minor quantities. Maier (1987a) quantified these as citraconic at 0.048-0.070%, 2-furoic at 0.009-0.0250%, itaconic at 0.013-0.020%, pyrrolidone carboxylic (pyroglutamic acid) at 0.06-0.10%, mesaconic at 0.005-0.013%, fumaric at 0.010-0.016% and maleic at 0.006-0.016%; a number of others were found at even lower levels, all in commercial roasted coffees. Tressl *et al.* (1978a) reported 2-furoic acid at 0.008% in an arabica roasted coffee.

The total content of major nonvolatile acids estimated by the Working Group from the data of van der Stegen and van Duijn (1987) is 276 mg/cup (assuming use of 10 g roasted coffee per cup), ranging from 246 to 300; the content estimated from the data of Maier (1987a), including phosphoric acid, averages 231 mg in arabica and 224 mg in robusta. These figures are somewhat higher than the average of 178 mg, including formic/acetic acids, given by Clinton (1985) on the basis of use of 7 g/cup.

Maier (1987a) regarded the combination of citric and acetic acids as the reason for the higher acidity of arabica than robusta coffee. Also significant for flavour is the relatively high amount of quinic acid lactone, which, like quinic acid itself, increases and decreases again with increasing severity of roasting, peaking at 0.7% on a dry basis (Clifford, 1985). Brews containing this compound and standing at elevated temperatures show increasing acidity, partly because this lactone is transformed into more quinic acid but also because the concentrations of some other acids increase (van der Stegen & van Duijn, 1987).

(vii) *Maillard reaction products (melanoidins)*

Products of the Maillard reaction are important constituents of roasted coffee; in a dry medium roast, they can comprise some 15-20%, of which 20-25% are hot water-soluble. At present, they are poorly characterized as caramelized products of sucrose and condensation products of polysaccharides with 'proteins' and other compounds (Trugo, 1985).

(viii) *Other compounds*

Clinton (1985) found reducing sugars at an average content per cup of 15 mg, other carbohydrates at 205 mg and peptides/'protein' at 62 mg.

(*b*) *Volatile substances*

The volatile compounds in coffee include carbonyl compounds, alcohols, acids, esters, terpenoid compounds, nitrogen- and sulfur-containing compounds, hydrocarbons, heterocyclic and aromatic compounds. The quantity (apart from the volatile aliphatic acids) obtained by distillation of roasted coffee is about 0.1% or 1000 mg/kg (Silwar *et al.*, 1986a). Volatile compounds are present in smaller amounts than in most other foods, but the range of types is greater.

The number of volatile components that have been identified has risen sharply over the last 20 years (Flament, 1987). The most up-to-date, complete listing of all identified components is that of Maarse and Visscher (1986) — now comprising over 700. An earlier listing by Vitzthum (1976) gave 550 volatile compounds (an English version is provided by Spiller, 1984a). Listings by Silwar *et al.* (1986a) and Flament (1987) give numbers only for categories of compounds. The systems of chemical grouping used differ somewhat in these lists, particularly with regard to sulfur-containing and furan-based compounds. The numbers of volatile compounds identified in roasted coffee are listed by group in Tables 19-22.

Those compounds that have been quantified have been listed by van Straten *et al.* (1983) and Silwar *et al.* (1986a,b). Only those detected by modern gas chromatography (GC)/mass spectrometry methods (i.e., published since about 1970) can be regarded as reliably identified, however. Contents are usefully given per cup of brew (standardized at 150 ml) or per litre, and suitable bases for calculation were given above.

Table 19. Classification of volatile compounds in roasted coffee: aliphatic benzenoid and alicyclic compounds[a]

Group/subgroup	Number identified			
	Total	Aliphatic	Benzenoid	Alicyclic
Hydrocarbons	73			
Saturated		24	9	1
Unsaturated		16	2 (in side chain)	1
Condensed polynuclear		–	20	–
Alcohols	20			
Saturated		12	2	1
Unsaturated		4	0	1
Aldehydes	29			
Saturated		11	5	0
Unsaturated		7	1	0
Hydroxy-		0	4	0
Alkoxy-		0	1	0
Ketones	69			
Mono-				
Saturated		23	2	2
Unsaturated		5	0	8
Hydroxy		6	3	0
Acyl-		0	0	1
Di-				
Saturated		13	1	5
Unsaturated		0	0	0
Acids	22			
Saturated		15	1	2
Unsaturated		4	0	0
Esters	29	23	6	0
Ethers	2	2	0	0
Acetal	1	1	0	0
Nitrogen-containing	21			
Amines		12	5	0
Nitriles		3	0	0
Oxime		1	0	0
Sulfur-containing	18			
Thiols		3	0	0
Thioethers (sulfides)				
Mono-		2	1	0
Di-		3	0	0
Tri-		2	0	0

Table 19 (contd)

Group/subgroup	Number identified			
	Total	Aliphatic	Benzenoid	Alicyclic
Sulfur-containing (contd)				
Thioester		1	0	0
Thioketone		1	0	0
Thiophenol		–	1	–
Miscellaneous (CS_2 etc.)		4	0	0
Phenols	40			
Mono-			1	
Alkylated		–	22	–
Alkoxy-		–	8	–
Dihydroxy benzenes		–	7	–
Trihydroxy benzenes		–	2	–
Total	324	198	104	22

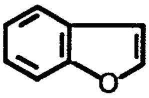
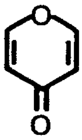
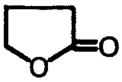
[a] From Maarse & Visscher (1986)

–, not applicable

Silwar *et al.* (1986a,b) stated that steam distillation of a medium-roasted arabica coffee released 700-800 ppm (mg/kg) by weight of 'aromatics', which corresponds to the 0.1% generally previously believed to be present, if acetic and formic acids are excluded. By GC analysis, they were able to account for 85-95% of this amount by summation of individually determined amounts: 170 compounds were found in the parts per million (milligrams per kilogram) range (1-150 ppm) and 70 in the parts per billion range (1-500 ppb); however, actual data were given for only 157 compounds. The greatest amount of the steam volatile complex by weight was contributed by heterocyclic compounds (80-85%), comprising furans of all kinds (at 38-45%), pyrazines (25-30%), pyridines (3-7%), pyrroles (2-3%), sulfur-substituted furans (0.4%), thiophenes (0.4%), thiazoles (0.15%) and oxazoles (< 0.01%). Only 3-5% by weight were aliphatic compounds, 3-5% were aromatic compounds and < 0.5% were alicyclic compounds.

A compilation of the data of Silwar *et al.* (1986a,b) is given in Table 23 to illustrate the expected content of volatile compounds per cup of brewed coffee. It is assumed that the extraction efficiency of home brewing is 100%, although in practice it is substantially less. Maarse and Visschler (1986) identified 715 compounds (see Tables 19-22).

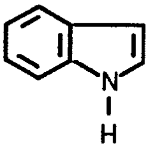
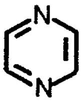
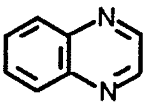
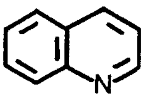
Table 20. Classification of volatile compounds in roasted coffee: heterocyclic (oxygen ring-containing compounds)[a]

Group/subgroup	Number identified						
	Total	Furans	Benzofurans	Pyrones	Pyrans	Lactones (maleic)	Anhydrides
							
Simple	5	1	1	0	0	3	0
Hydrogenated	8	5	1	0	2	0	0
Alkyl-	42	29	1	3	0	6	3
Alkoxy-	1	1	0	0	0	–	–
Aryl-	1	1	0	0	0	–	–
Difuryl	8	8	0	–	–	–	–
Aldehydes	6	6	0	–	–	–	–
Ketones (including hydrogenated)	15						
Mono-		10	0	–	–	–	–
Di-		5	0	–	–	–	–
Acyl-	9	9	0	–	–	–	–
Alcohols	2	2	0	–	–	–	–
Acid	1	1	0	–	–	–	–
Esters	11	11	0	–	–	–	–
Ethers	4	4	0	–	–	–	–
Sulfur-containing	18						
Thiols		2	0	–	–	–	–
Thioethers		14	0	–	–	–	–
Thioester		1	0	–	–	–	–
Thioketone		1	0	–	–	–	–
Total	131	111	3	3	2	9	3

[a] From Maarse & Visscher (1986)

–, not applicable

Table 21. Classification of volatile compounds in roasted coffee: heterocyclic (nitrogen ring-containing compounds)[a]

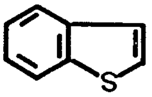
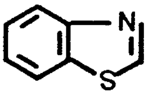
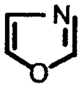
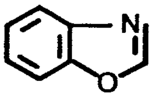
Group/subgroup	Number identified						
	Total	Pyrroles	Benzo-pyrroles (indoles)	Pyrazines	Benzo[*a*]-pyrazines (quinoxalines)	Pyridines	Benzo[*b*]-pyridines (quinolines)
							
Simple	6	1	1	1	1	1	1
Hydrogenated	9	2	1	0	5	1	0
Alkyl-	77	28	2	34	4	6	3
Furfuryl-	27	14	0	13	0	0	0
Aryl-	1	1	0	0	0	0	0
Acyl-	30	20	0	7	0	3	0
Alkoxy-	4	0	0	4	0	0	0
Ketones (mono- and di-)	3	2	1	0	0	0	0
Alicyclic	12	0	0	12	0	0	0
Other	2	0	0	0	1	1	0
Total	171	68	5	71	11	12	4

[a] From Maarse & Visscher (1986)

(i) *Carbonyl compounds* (Table 24)

Maarse and Visscher (1986) listed 18 aliphatic aldehydes in freshly roasted coffee, in a saturated series up to heptanal, including seven unsaturated but no alicyclic compounds. *trans*-2-Nonenal is believed to be present in a very small amount. Glyoxal, methylglyoxal and ethylglyoxal are not listed as being present in roasted coffee by Maarse and Visscher (1986) and were not quantified by Silwar *et al.* (1986a) using a direct, non-derivative GC method; however, methylglyoxal has been detected by indirect GC methods (Kasai *et al.*, 1982; Hayashi & Shibamoto, 1985; Nagao *et al.*, 1986a; Shane *et al.*, 1988; Aeschbacher *et al.*, 1989) (Table 25; see also the monograph on methylglyoxal, p. 446).

Table 22. Classification of volatile compounds in roasted coffee: heterocyclic (sulfur, sulfur/nitrogen and nitrogen/oxygen ring–containing compounds)[a]

Group/subgroup	Number identified						
	Total	Thiophenes 	Benzothiophenes 	Thiazoles 	Benzothiazoles 	Oxazoles 	Benzoxazoles 
Simple	4	1	1	1	1	0	0
Hydrogenated	1	0	0	0	0	1	0
Alkyl-	56	7	0	23	0	20	5
Di-		1	0	0	0	0	0
Aryl-	2	1	0	0	0	1	0
Ketones	5	5	0	0	0	0	0
Acyl-	13	9	0	2	0	2	0
Alcohols	1	1	0	0	0	0	0
Esters	3	3	0	0	0	0	0
Other	4	4	0	0	0	0	0
Total	89	32	1	26	1	24	5

[a] From Maarse & Visscher (1986)

Table 23. Volatile compounds in coffee brewed from 10 g medium-roasted arabica coffee[a]

Group	Number identified	Number quantified	Total (mg/cup)[b]
Carbonyls	≥97 26 furanoid	≥12 18 furanoid	0.10–0.20 1.30–1.91
Volatile acids	≥21 1 furanoid	≥ 2 1 furanoid	65 (mainly acetic acid)
Alcohols	≥20 2 furanoid	≥ 5 2 furanoid	0.9–1.35 (mainly furfuryl alcohol)
Esters, lactones and ethers	≥40 15 furanoid	≥ 0 7 furanoid	< 0.07
Pyrroles	≥66 4 indoles	≥14 2 indoles	0.13–0.16
Pyrazines	71	28	1.7–2.2
Pyridines	10	2	
Furans (not already included)	45	21	< 0.04
Phenols and phenol ethers	40	9	0.12–0.29

Table 23 (contd)

Group	Number identified	Number quantified	Total (mg/cup)[b]
Sulfur compounds	95	21	0.1
Others	139	14	Very small
Total	≥692	158	< 4.46–6.11 (excluding acids)

[a] Adapted from Silwar *et al.* (1986a,b)
[b] Calculated by the Working Group

Table 24. Contents of carbonyls in roasted coffee (mg/kg)

Compound	Content[a] (ppm; mg/kg)	Reference
Aldehydes		
Aliphatic		
3-Methyl butanal	6.7	van Straten *et al.* (1983)
n-Hexanal	0.3–0.7	Silwar (1982)
Benzenoid		
Benzaldehyde	1.8, 0.7–1.10	Silwar (1982); Silwar *et al.* (1986a)
3,4-Dihydroxybenzaldehyde	8–20	Tressl *et al.* (1978a)
4-Hydroxy-3-methoxybenzaldehyde (vanillin)	2–3	Tressl *et al.* (1978a)
3,4-Dihydroxycinnamaldehyde	5–12	Tressl *et al.* (1978a)
2-Phenylbut-2-enal	0.6, 0.1–0.20	Silwar (1982); Silwar *et al.* (1986a)
2-Phenylacetaldehyde	3.7, 1.5–2.0	Silwar (1982); Silwar *et al.* (1986a)
Furanoid		
Furfural	5.2–232, 55–80	Silwar (1982); Silwar *et al.* (1986a)
5-Methylfurfural	216, 50–70	Silwar (1982); Silwar *et al.* (1986a)
5-(Hydroxymethyl)-2-furfural	10–35	Tressl *et al.* (1978a)
(2-Furyl)acetaldehyde	0.5	Silwar (1982)
Ketones and diketones		
Aliphatic		
1-Hydroxypropan-2-one	4, 0.25–0.30	Silwar (1982); Silwar *et al.* (1986a)
3-Hydroxybutan-2-one	4.9, 0.25–0.35	Silwar *et al.* (1986a)
2,3-Butanedione (diacetyl)	2.7, 0.05–0.15	Silwar *et al.* (1986a)
2-Pentanone	0.4–4.3	Silwar (1982)
4-Methylpentan-2-one	6.5	Silwar (1982)
2-Hydroxypentan-3-one	5.2, 0.05–0.15	Silwar (1982); Silwar *et al.* (1986a)

Table 24 (contd)

Compound	Content[a] (ppm; mg/kg)	Reference
Ketones and diketones (contd)		
Aliphatic (contd)		
2,3-Pentanedione	1.0–3.0	Silwar *et al.* (1986a)
5-Methylhexan-2-one	0.5	Silwar (1982)
2,3-Hexanedione	3.2, 0.3–0.5	Silwar (1982); Silwar *et al.* (1986a)
3-Heptanone	0.4	Silwar (1982)
4-Heptanone	0.5	Silwar (1982)
2-Pentadecanone	2.9, 0.10–0.15	Silwar (1982); Silwar *et al.* (1986a)
1-Acetoxy-2-propanone	2.0–5.0	Silwar *et al.* (1986a)
1-Acetoxy-3-butanone	2.0–4.0	Silwar *et al.* (1986a)
1-Acetoxy-2-butanone	2.0–3.0	Silwar *et al.* (1986a)
Benzenoid		
2-Hydroxyacetophenone	1.6	Silwar (1982)
Alicyclic		
3-Methylcyclopentane-1,2 dione (3-Methyl-2-hydroxycyclo-pent-2-ene-1-one) (cyclotene)	17–40	Tressl *et al.* (1978a)
Furanoid		
2-Methyltetrahydrofuran-3-one	10.0–16.0	Silwar *et al.* (1986a)
2,4-Dimethyl-2*H*-furan-3-one	0.50–0.60	Silwar *et al.* (1986a)
2,5-Dimethyl-2*H*-furan-3-one	10.7	Silwar (1982)
2,5-Dimethyl-4-hydroxy-2*H*-furan-3-one (furaneol)	25–50	Tressl *et al.* (1978a)
2,5-Dimethyl-4-ethoxy-2H-furan-3-one	2–8	Tressl *et al.* (1978a)
2-Acetylfuran	24.1–31.4	Silwar (1982)
	6.0–12.00	Silwar *et al.* (1986a)
2-Acetonylfuran	2.2	Silwar (1982)
2-Propionylfuran	0.5, 1.10–1.50	Silwar (1982); Silwar *et al.* (1986a)
1-(2-Furyl)butan-2-one	1.4, 0.10–0.20	Silwar (1982); Silwar *et al.* (1986a)
4-(2-Furyl)butan-2-one	4.6, 0.10–0.15	Silwar (1982); Silwar *et al.* (1986a)
1-(5-Methyl-2-furyl)butan-2-one	0.8, 0.25–0.35	Silwar (1982); Silwar *et al.* (1986a)
4-(5-Methyl-2-furyl)butan-2-one	0.25–0.30	Silwar *et al.* (1986a)
1-(2-Furyl)pentan-1,2-dione	1.0, 0.05–0.10	Silwar (1982); Silwar *et al.* (1986a)
2-Acetyl-5-methylfuran	0.5–1.0	Silwar *et al.* (1986a)
2-Methyl-5-propionylfuran	4.2	Silwar (1982)
1-(2-Furyl)-propane-1,2-dione	3.9, 0.10–0.15	Silwar (1982); Silwar *et al.* (1986a)
1-(5-Methyl-2-furyl)propane-1,2-dione	3.4, 0.25–0.30	Silwar (1982); Silwar *et al.* (1986a)

Table 24 (contd)

Compound	Content[a] (ppm; mg/kg)	Reference
Ketones and diketones (contd)		
Furanoid (contd)		
1-(2-Furyl)butane-1,2-dione	3.3, 0.10–0.15	Silwar (1982); Silwar *et al.* (1986a)
1-(5-Methyl-2-furyl)butane-1,2-dione	1.4, 0.05–0.10	Silwar (1982); Silwar *et al.* (1986a)

[a] One figure is given for one sample; Silwar *et al.* (1986a) tested five commercial samples of roasted arabica coffee, while Silwar (1982) and Tressl *et al.* (1978a) tested numerous samples of arabica and robusta coffee.

Table 25. Contents of methylglyoxal in coffee

Content			Reference
Roasted coffee (mg/kg)	Brewed coffee		
	Amount	Conditions	
[58–75]	470–730 μg/cup	8 g/100 ml	Kasai *et al.* (1982)
25	76 μg	3 g/180 ml	Hayashi & Shibamoto (1985)
–	7 μg/ml	10 g/150 ml	Nagao *et al.* (1986a)
–	273–341 μg/g (filtered coffee)	25 g/250 ml	Shane *et al.* (1988)
[21–39][a]	106–197 μg/g dried product	1 g/10 ml	Aeschbacher *et al.* (1989)

[a] Calculated assuming extraction yield of 20% dry soluble solids in the brew

van Straten *et al.* (1983) reported quantitative data on only two of the 18 aldehydes. While acetaldehyde has been reported repeatedly as being present, no reliable quantitative data appear to be available. Hayashi *et al.* (1986) reported a level of 3.4-4.5 ppm (mg/l) formaldehyde (see IARC, 1982, 1987) in brewed coffee.

Maarse and Visscher (1986) listed 11 benzenoid aldehydes; van Straten *et al.* (1983) reported quantitative data on five of them, including 3,4-dihydroxybenzaldehyde at 8-20 ppm (mg/kg) and benzaldehyde at 1.8 ppm (mg/kg). The later work of Silwar *et al.* (1986a), which was not in this listing, generally reported lower levels of all carbonyls quantified in a medium-roasted arabica coffee and a lower level of benzaldehyde, and included 2-phenylacetaldehyde (1.5-2 mg/kg).

Other important aldehydes present are furanoid (six quantified by van Straten *et al.*, 1983); in particular, furfural has been found at up to 255 ppm (mg/kg) [equivalent to 2.6 mg/cup] and 5-methylfurfural at up to 216 ppm (mg/kg; Silwar, 1982). However, Silwar *et al.* (1986a) reported much lower quantities (up to 80 and 70 ppm (mg/kg), respectively).

Maarse and Visscher (1986) list 47 aliphatic and 16 alicyclic ketones, including diketones, three acetophenones, two benzenoid ketones and one benzenoid diketone. van Straten *et al.* (1983) reported quantitative data on 14 of these, although only 3-methylcyclopentane-1,2-dione (cyclotene) is present at significant amounts of 17-40 ppm (mg/kg; Tressl *et al.* (1978a). This compound was not reported by Silwar *et al.* (1986a). Diacetyl (2,3-butadione) was present at 2.7 ppm (mg/kg; Silwar, 1982), but Silwar *et al.* (1986a) reported only 0.05-0.15 ppm (mg/kg) diacetyl [equivalent to 0.5-15 μg/cup]. They also gave data on 10 aliphatic ketones, three benzenoid aldehydes and 14 furanoid ketones.

Strictly speaking, a number of other pyrrole-based carbonyls could be included; but these are described with nitrogen compounds, and the quantities involved are small. Isomaltol (2-acetyl-3-hydroxyfuran) has been found in arabica and robusta coffees at levels of 8 and 1.5 ppm (mg/kg), respectively (Tressl *et al.*, 1978a).

(ii) *Alcohols*

Maarse and Visscher (1986) listed 18 basic aliphatic and alicyclic alcohols and two aromatic alcohols; van Straten *et al.* (1983) quoted quantitative amounts for only four of them.

Furfuryl alcohol (grouped by Maarse & Visscher (1986) in the furan group) is the most prevalent volatile compound in roasted coffee (except acetic acid), with reported levels of 300 ppm (mg/kg) in arabica and 520 ppm (mg/kg) in robusta (Tressl *et al.*, 1978a), up to 881 ppm (mg/kg; van Straten *et al.*, 1983) and 678 ppm (mg/kg; Silwar, 1982). 5-Methylfurfuryl alcohol was reported at 25 ppm (mg/kg; Silwar, 1982). Silwar *et al.* (1986a) later reported levels of 90-135 ppm (mg/kg) furfuryl alcohol and 1.2-1.8 ppm (mg/kg) 5-methylfurfuryl alcohol. Furfuryl alcohol is regarded as detrimental to the flavour of coffee.

(iii) *Acids*

Maarse and Visscher (1986) listed 19 volatile acids in an aliphatic series up to decanoic, one benzoic and two alicyclic. The quantitative data quoted by van Straten *et al.* (1983) are derived from Kung *et al.* (1967), but the later data of Blanc (1977), Maier (1987a) and van der Stegen and van Duijn (1987) are more reliable (Table 26). The total content of formic and acetic acids found by van der Stegen and van Duijn (1987) would be 6500 ppm [which amount to about 65 mg per cup].

Table 26. Volatile acid content of dry roasted coffees

Coffee	Content (%)		Reference
	Formic acid	Acetic acid	
Colombian and Santos robusta	0.066–0.140	0.25–0.33	Kung *et al.* (1967)
Kenya arabica (very dark to very light)	–	0.4–0.09	Blanc (1977)
Arabica (average of 4 samples, peak value)[a]	0.23	0.60	Maier (1987a)
Robusta medium roast (average of 4 samples)[a]	0.23	0.54	Maier (1987a)
17 commercial coffees (average and range)	0.22 (0.18–0.25)	0.43 (0.36–0.55)	van der Stegen & van Duijn (1987)

[a] Calculated by the Working Group
–, not tested

Kung *et al.* (1967) reported the presence of nine other acids in relatively low quantities. Silwar *et al.* (1986a) gave levels only for 2-methylbutanoic acid, at 25.0-40.0 ppm (mg/kg).

(iv) *Esters, ethers and lactones*

Maarse and Visscher (1986) reported the presence of 23 aliphatic, six benzenoid esters and 11 furanoid-based esters. None of these is reported to be present in any substantial amount; methyl salicylate is reported at 1.4 ppm (mg/kg) and furfuryl acetate at 16.3 ppm (mg/kg; Silwar, 1982) or 3.5-5.5 ppm (mg/kg; Silwar *et al.*, 1986a), but there are few other quantitative data. Six ethers and nine lactones are listed by Maarse and Visscher (1986), and are reported in relatively small amounts by Silwar *et al.* (1986a).

(v) *Nitrogen compounds*

Amines and amides: Maarse and Visscher (1986) listed the presence of 12 aliphatic amines; van Straten *et al.* (1983) reported quantitatively only on dimethylamine at 2 ppm (mg/kg) and on five aromatic amines. One imide, *N*-α-dimethylsuccinimide (Maarse & Visscher, 1986), and the secondary amine, pyrrolidine (Singer & Lijinsky, 1976), have been reported.

N-N/S- *and* N/O-*Heterocyclic compounds*: This is an important group of compounds with regard to the flavour of roasted coffee. Maarse and Visscher (1986) listed the presence of 71 pyrazines, 12 pyridines, four quinolines, 11 quinoxalines, 26 thiazoles, 24 oxazoles, 68 pyrroles and five indoles.

A considerable amount of quantitative data was reported by Tressl *et al.* (1981) and van Straten *et al.* (1983) on 44 of the pyrroles and 25 of the pyrazines. The quantities of individual pyrroles are quite low (in general < 1 ppm), although levels of 1.1-2.7 ppm (mg/kg) pyrrole itself and 17 ppm (mg/kg) 2-formyl-1-methylpyrrole were reported. Some pyrazines occur at higher levels (104 ppm (mg/kg) methyl pyrazine), but most are found at lower levels (acetyl pyrazine, 1.3 ppm (mg/kg)). Pyridine was reported to be present at up to 49 ppm (mg/kg; van Straten *et al.*, 1983). Quantitative data on 18 pyrroles (including 13 carbonylic) give a total of 79 ppm (mg/kg); 2 ppm (mg/kg) were found for two indoles and 395 ppm for 28 pyrazines (Silwar, 1982). Silwar *et al.* (1986a) provided quantitative data on 28 pyrazines (170-218 mg/kg), two pyridines, 14 pyrroles (mainly carbonylic, 12.6-15.0 mg/kg) and two indoles.

2-Amino-3,4-dimethylimidazo[4,5-*f*]quinoline (MeIQ) (see IARC, 1986b) has been detected in coffee beans at 16 ng/kg (hot-air-roasted), 32 ng/kg (charcoal-roasted) and 150 ng/kg (high-temperature-roasted) only after alkaline hydrolysis (Kikugawa *et al.*, 1989; Takahashi *et al.*, 1989).

S- *and* O/S-*Heterocyclic compounds*: Maarse and Visscher (1986) reported the presence of 28 thiophenes and two dithiolanes and provided some quantitative data; none occurs in apparently significant amounts. Silwar (1982) found six thiophenes at a total content of 8.9 ppm (mg/kg) and one dithiolane at 3.7 ppm (mg/kg). Silwar *et al.* (1986b) reported the total content of six thiophenes at 4.7 ppm (mg/kg) in roasted Colombian arabica and 3.2 in roasted robusta coffee.

(vi) *Furan-based compounds*

Maarse and Visscher (1986) reported the presence of 92 furan compounds and a further 18 sulfur-containing furan compounds, many of which have been mentioned previously (as aldehydes, ketones and esters). Furfurylthiols (furfuryl mercaptans) and sulfides appear to be especially important with regard to flavour but are present in only small absolute quantities, e.g., furfurylthiol at 2.2 ppm (mg/kg) in roasted robusta, at 1.1 ppm (mg/kg) in arabica (Tressl & Silwar, 1981), at 1.65 ppm (mg/kg) in roasted Ivory Coast robusta and at 0.9 ppm (mg/kg) in roasted Colombias (Silwar *et al.*, 1986b). The total content of ten sulfur-containing furans was only 2.5-6.4 ppm (mg/kg; van Straten *et al.*, 1983). The total content of 17 furans was 41 ppm (mg/kg), with 2-acetylfuran contributing 31.4 ppm (Silwar, 1982; van Straten *et al.*, 1983). Kahweofuran (2-methyl-3-oxa-8-thiabicyclo(3.3.0)-1,4-octadiene), of particular importance in flavour, has been reported at 1.75 ppm (mg/kg) in roasted Colombian arabicas, at 2.0 ppm (mg/kg) in Kenyan coffees and at 0.45 ppm (mg/kg) in roasted Ivory Coast robustas (Silwar *et al.*, 1986b).

(vii) *Other sulfur compounds*

A number of other aliphatic and aromatic sulfides, including di- and trisulfides, are especially important in the aroma of dry roasted coffee. Maarse and

Visscher (1986) listed 14 aliphatic and two aromatic sulfides. The quantities involved are very small; e.g., dimethyldisulfide was found at 0.01 ppm (mg/kg) in roasted Colombian arabica and at 0.1 ppm in roasted Ivory Coast robustas (Tressl & Silwar, 1981; Silwar *et al.*, 1986b).

(viii) *Phenols*

Phenols are another important group of flavour compounds; 39 were listed by van Straten *et al.* (1983). Quantitative determinations were reported by Tressl (1977), Tressl *et al.* (1978a,b), van Straten *et al.* (1983) and Silwar *et al.* (1986a). Silwar *et al.* (1986a) reported on the contents of 13 phenols (excluding dihydroxy- and trihydroxybenzenes) in a medium-roasted arabica. The actual quantities present are again small; the differences between roasted robusta and arabica are shown in Table 27. When arabica coffee is roasted very darkly, greater quantities of some phenols have been found, e.g., the phenol content increased from 13 to 63 ppm (mg/kg) and that of guaiacol from 2.7 to 10.6 ppm (Tressl *et al.*, 1978b).

(ix) *Pyrones*

Three pyrones have been identified and quantified by Tressl *et al.* (1978a) and reported by van Straten *et al.* (1983; Table 28).

(x) *Hydrocarbons*

Seventy-three hydrocarbons have been identified in roasted coffee (Maarse & Visscher, 1986); 11 have been quantified at the parts per billion (micrograms/kilogram) level and four at the parts per million (milligrams/kilogram) level (van Straten *et al.*, 1983).

As both roasted and instant coffee are derived by roasting procedures (at temperatures of the order of 210°C, with higher air temperatures), polycyclic aromatic hydrocarbons (PAH), and in particular benzo[*a*]pyrene, can be expected to be present. Numerous studies have been conducted on their actual occurrence (e.g., Ruschenburg, 1985; de Kruijf *et al.*, 1987; reviewed by Strobel, 1988a). Determinations in roasted coffee, best done by high-performance liquid chromatography (HPLC) and fluorimetric techniques, suggest a range of <0.1-1.2 μg/kg, with an average of 0.3 μg/kg; however, PAH are largely removed in the spent grounds (e.g., on filter papers), leading to contents in the brews of <0.01 μg/l (Ruschenburg, 1985) or 0.0003-0.0008 μg/l (de Kruijf *et al.*, 1987). Darker roasts produce slightly higher values. It has been shown that the chaff produced during roasting contains much higher levels (2-23 μg/kg) (de Kruijf *et al.*, 1987); although this material is usually discarded, it is sometimes mixed in with subsequently ground roasted coffee. Strobel (1988a) calculated that coffee consumption contributes $<0.1\%$ (or 0.25 μg per year per person) of the total PAH inhaled or ingested from all sources.

Table 27. Phenol content of roasted coffees[a]

Phenolic compound	Content (mg/kg)		
	Arabica	Robusta	Not stated
Phenol	13, 1.20–2.20[b]	17	60
2-Methylphenol (*ortho*-cresol)	1.2, 0.70–1.10[b]	1.1	12.4
3-Methylphenol (*meta*-cresol)	0.7, 0.15–0.50[b]	1.2	7.4
4-Methylphenol (*para*-cresol)	1.3, 0.30–0.60[b]	1.0	13.2
2-Ethylphenol			1.7
3-Ethylphenol			1.3
4-Vinylphenol	0.2	0.2	0.6
2,3-Dimethylphenol			2.1
2,4-Dimethylphenol			2.0
2,5-Dimethylphenol			1.5
2,6-Dimethylphenol			0.2
3,4-Dimethylphenol			0.8
2-Ethyl-4-methylphenol			1.0
4-Ethyl-2-methylphenol			0.9
Ethylmethylphenol			0.4
2-Propyl-4-methylphenol			0.2
Methylpropylphenol			0.2
2,3,5-Trimethylphenol			0.3
2,4,5-Trimethylphenol			0.3
2,3,6-Trimethylphenol			0.2
1,2-Dihydroxybenzene (pyrocatechol)	80	120	
1,4-Dihydroxybenzene (hydroquinone)	40	30	
1,2-Dihydroxy-3-methylbenzene		9[c]	
1,2-Dihydroxy-4-methylbenzene	16	13	
1,2-Dihydroxy-4-ethylbenzene	37	80	
1,2-Dihydroxy-4-vinylbenzene	25	25	
2-Methoxyphenol (guaiacol)	2.7, 2-3[b]	8.4	10.6
4-Methyl-2-methoxyphenol	0.01–0.02[b]		0.1
4-Ethyl-2-methoxyphenol	0.8-1.50[b]		2.2
4-Vinyl-2-methoxyphenol	9.5, 8-20.0[b]	19.5	7.9
4-Propenyl-2-methoxyphenol (isoeugenol)			0.1
1,2-Dimethoxy-4-vinylbenzene	0.40–0.80[b]		3[d]
1,2,4-Trihydroxybenzene	20	13	
1,2,3-Trihydroxybenzene (pyrogallol)	45	55	

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[a] Data from Tressl *et al.* (1978a,b) unless noted otherwise

[b] From Silwar *et al.* (1986a)

[c] From van Straten *et al.* (1983)

[d] From Silwar (1982)

Table 28. Pyrone content of roasted coffees[a]

Pyrone	Content (mg/kg)	
	Arabica	Robusta
3-Hydroxy-2-methyl-4-pyrone (maltol)	39	45
5,6-Dihydro-3,5-dihydroxy-2-methyl-4-pyrone (or 5,6-dihydro-5-hydroxymaltol)	13	10
3,5-Dihydroxy-2-methyl-4-pyrone (5-hydroxymaltol)	15	6

[a] From Tressl *et al.* (1978a)

(xi) *Other compounds*

Hydrogen peroxide has been found in roasted coffee (Fujita *et al.*, 1985a).

(*c*) *Compounds in instant coffee*

The quantitative data presented refer generally to dry instant coffee (powder or granules). To obtain representative values for the content in the beverage, it is convenient and realistic to assume use of 2 g instant coffee per 150-ml cup. With 100% solubility, the content in milligrams per kilogram for a given component of instant coffee should be divided by 500 to give the content in milligrams per cup.

(i) *Nonvolatile substances*

Caffeine and other purines: Caffeine levels have been determined directly in 12 commercial samples using HPLC methods (Trugo *et al.*, 1983); the range was 28-48 g/kg [which would correspond to 56-92 mg/cup]. The higher level resulted from higher levels of robusta in the blend. The caffeine contents of instant coffees manufactured in Brazil are somewhat lower: Angelucci *et al.* (1973), using a spectrophotometric method on 15 arabica samples, reported levels of 1.63-3.86%, with one robusta containing 4.64%. Minute amounts of the other alkaloids that occur in roasted and green coffees also appear in instant coffee, at approximately half the amount.

Chlorogenic acids and related substances: Trugo and Macrae (1984b) determined by HPLC the chlorogenic acid content of 13 commercial instant coffees bought in the UK. Total chlorogenic acids ranged from 3.61 to 10.73%; the levels were 2.55-7.64% for total caffeoylquinic acids, 0.16-0.58% for total dicaffeoylquinic acids and 0.74-1.93% for total feruloyl quinic acids. The levels found depended on the extraction conditions and on differences between varieties. Data from other workers (summarized by Clifford, 1985) showed a similar range for total chlorogenic acids; Maier (1987a) found [2.7-8.9%] in five samples. The lower figures resulted from use of darkly roasted coffees. The Working Group estimated that these values correspond to 54-215 mg/cup.

Glycosides: Viani (1988) estimated the content of atractyligenin at 0.8-0.9 mg/cup of arabica instant coffee and negligible for robusta.

Lipids: Instant coffees are generally free of lipids (and therefore the diterpenes, kahweol and cafestol), but many commercial brands are plated with about 0.3-0.5% coffee oil obtained by expression from roasted coffee or other methods to provide headspace aroma. Viani (1988) reported 0.02% oil and 0.0002% diterpenes in nonaromatized powder and 0.3% and 0.02%, respectively, in aromatized powder, corresponding to 0.4 mg/cup oil and 0.004 mg/cup diterpenes in nonaromatized powder and 7 mg/cup oil and 0.4 mg/cup diterpenes in aromatized powder. Certain commercial brands of instant coffee contain up to 10% by weight of very finely ground roasted coffee; this will increase these figures by 1.6% oil and 0.12% diterpenes in the powder, or 32 and 2.4 mg/cup, respectively, making this brew comparable with an espresso-type brew.

Trigonelline and nicotinic acid: Trigonelline has been determined in 12 UK commercial dry instant coffees by HPLC; an average of 1.37% (range, 0.94-1.69%) was found (Trugo *et al.*, 1983), [corresponding to 20-35 mg/cup, although the data on roasted coffee would suggest figures of 8-44 mg/cup]. Viani (1988) reported trigonelline at 5-15 mg/cup in 22 samples, which were therefore probably darkly roasted. In the same samples, nicotinic acid was found at 0.2-1.2 mg/cup; the data for roasted coffee suggest similar levels [0.4-1.6 mg/cup].

Acids: Of the nonvolatile acids, quinic, citric, malic and pyruvic acids are known to be present in fairly large quantities. Blanc (1977) reported on the total quantity of citric, malic, lactic and pyruvic acids and of the volatile acetic acid in instant coffees from four different countries. A range of 1.5-4.9% was found, which suggests that the acid content is increased only slightly as a consequence of industrial processing from roasted to dried extracts. Any increase occurring during extraction is balanced by loss during drying. Schormüller *et al.* (1961) reported average values of 2.20% citric acid, 0.50% malic acid, 0.45% lactic acid, 0.95% acetic acid and 0.08% pyruvic acid in dry instant coffee, to give a total of 4.18%, suggesting a marked increase in the level of acetic acid. Instant coffees derived from medium-roasted arabica coffee tend to have higher acid contents than darkly roasted robusta. Average levels of 3.8% (German instant coffees) and 2.3% (French instant coffee) result in [76 and 46 mg/cup], respectively.

Trace elements: The main mineral element in roasted and instant coffee is potassium, and levels can range from 3.6 to 5.9% in dry instant coffee (Clarke, 1985). Maier (1981) compiled data on all other elements present or likely to be present. In instant coffee, trace elements can originate both from the roasted coffee and from the water used for extraction: the content in the water can be at least tripled during evaporation and drying of the extracts to the final product. Instant coffee is manufactured almost entirely in stainless-steel equipment, from which contamination is minimal (Clarke, 1985).

Other components: As a consequence of industrial extraction, higher percentages of melanoidins (see p. 71), polysaccharides and 'proteins' are found in instant coffee than in the soluble part of brewed coffee. Dissolution of a greater amount of polysaccharides is accompanied by some cleavage into constituent monoses, indicated by the presence of small quantitites of arabinose, galactose and mannose (Trugo, 1985).

(ii) *Volatile compounds*

Little quantitative information and few comprehensive listings are available of the volatile compounds present in commercial instant coffee. Certain volatile compounds, particularly sulfides and other non-polar substances, that occur preferentially in the oil of roasted coffee rather than in the carbohydrate matrix will be present as a result of 'aromatization' with coffee oil. Over 80 volatile compounds were identified in a commercial freeze-dried brew, including thiazoles, thiophenes, pyridines, pyrroles, pyrazines and furfurals (Dart & Nursten, 1985); the preparation was relatively rich in the latter two groups of compounds. In general, the volatile compounds found in brewed coffee can be expected to occur, to a greater or lesser extent.

Carbonyls: Methylglyoxal has been quantified in instant coffee by derivative GC (see also the monograph on methylglyoxal, p. 445), at levels of 23 ppm (μg/g; Hayashi & Shibamoto, 1985), 404-994 ppm (Shane *et al.*, 1988) and 70-217 ppm (Aeschbacher *et al.*, 1989). Kasai *et al.* (1982) found 100-150 μg/cup assuming 1.5 g of instant coffee for 100 ml water. Aeschbacher *et al.* (1989) also reported the presence of 13-42 μg/g diacetyl and 5-25 μg/g glyoxal in dry product.

Acids: The volatile and nonvolatile acid content of instant coffee is discussed above (pp. 80 and 86).

Esters: Methyl salicylate was found at 0-8.4 mg/l in nine samples of instant coffee (2 g powder/100 ml water; Swain *et al.*, 1985).

Furan- and sulfur-based compounds: Some compounds containing sulfur were quantified in instant coffee: furfuryl thiol, 3.90 ppm (mg/kg); 5-methyl furfuryl methyl disulfide, 0.015 mg/kg; and kahweofuran, 0.60 mg/kg. Three other furans have also been quantified (Tressl & Silwar, 1981). In general, these figures are comparable with those for roasted coffee, but when they are calculated as milligrams per cup they are quite low [e.g., kahweofuran, 1.2 μg/cup].

Pyrones: Tressl (1980) found more maltol (60-120 ppm (mg/kg)) than was expected.

Other compounds: Hydrogen peroxide has been detected at 180 ppm (mg/kg) in instant coffee (Aeschbacher *et al.*, 1989), and formaldehyde was found at 10-16.3 ppm (Hayashi *et al.*, 1986). Cyclotene, found at 70-110 mg/kg, occurred at a higher level than would have been expected from roasted coffees (Tressl, 1980).

No data were available to the Working Group on alcohols, nitrogen compounds, other sulfur compounds or phenols.

(*d*) *Compounds in decaffeinated coffee*

Under the Directives of the Commission of the European Communities (1977, 1985), dry decaffeinated instant coffees must contain no more than 0.3% caffeine; in practice, they contain less. This figure corresponds to 0-6 mg/cup of instant coffee brew, which also corresponds to that found (Barone & Roberts, 1984).

The solvents used in decaffeination may remove small quantities of aroma precursors, e.g., trigonelline, or increase their levels, e.g., amino acids and reducing sugars.

(*e*) *Additives and contaminants*

(i) *Flavouring additives*

Both roasted and instant coffees are largely marketed throughout the world as 100% pure coffee products, and are clearly labelled as such in developed countries (Commission of the European Communities, 1985). Blends are also available with many different kinds of roasted plant products, including chicory and malted and unmalted barley. Worldwide consumption in 1985 of dried chicory roots was estimated at 128 000 tonnes per annum, of which 32% was consumed in France, 55% in other European countries and 12% in South Africa. After roasting, chicory is mixed with both roasted and instant coffee, but no information was available on the quantities used. The quantities consumed annually of mixtures with barley vary considerably, in relation to the cost of coffee (Maier, 1987b).

(ii) *Other additives*

Preservatives are not used. Occasionally, roasted and instant coffees have been used as vehicles for vitamins and minerals. Flow agents (sodium aluminium silicates) may be incorporated in instant coffees used in vending machines (by national derogation in the Directive of the Commission of the European Communities).

(iii) *Contaminants*

For the purpose of this section of the monograph, the term 'contaminants' is used to mean those constituents sometimes present in the products, and therefore in the beverages derived from them, which are not essential to the flavour and properties of the beverage. Some of these potential contaminants have known toxicological and, in some cases, carcinogenic effects.

Mycotoxins: Numerous studies, especially since 1965, have been conducted on the occurrence of mycotoxins in green coffee, and therefore in roasted and brewed coffee, due to the presence of mouldy beans. These studies were reviewed comprehensively by Strobel (1988b) and more briefly by Viani (1988). In particular, aflatoxin B_1 (see IARC, 1976a, 1987), ochratoxin A (see IARC, 1983, 1987) and, less often, sterigmatocystin (see IARC, 1976b) have been found in consignments of green coffees containing mouldy beans, although regulations seek to prevent such importation. Levels of aflatoxin B_1 at 3-12 ppb (μg/kg) in 2% of samples analysed, of ochratoxin A at 0.5-360 ppb in 3.5% of samples, and of sterigmatocystin at 1140 and 12 000 ppb in two very mouldy samples have been measured in some 2000 consignments examined. Decaffeinated green coffee beans that have been allowed to go mouldy show a greater tendency to develop toxins than nondecaffeinated coffee on account of the absence of the inhibitory action of caffeine. Ochratoxin A was found to be largely destroyed (80-99%) on roasting, as was aflatoxin B_1, to a slightly lesser extent.

Pesticides: Coffee beans are protected from pests within the cherry by direct application of pesticides, details of which have been reported (Mitchell, 1988; Snoeck, 1988). Coffee itself is consumed in the producing countries only after further processing, including roasting and brewing or extracting, which eliminate these contaminants almost quantitatively. Viani (1988) compiled available data on α- and β-hexachlorocyclohexanes, lindane, the DDT group, aldrin, dieldrin and others. Of six instant coffee samples, one contained 1.2 ng/g total hexachlorocyclohexanes and one contained 3 ng/g lindane, but no other pesticide was found. In contrast, 15 of 150 samples of green coffee had traces up to 290 ng/g lindane.

Nitrosamines: *N*-Nitrosopyrrolidine (see IARC, 1978) was found in five of ten instant coffees at 0.3-1.4 ppb (μg/kg) by Sen and Seaman (1981). The presence of this nitrosamine has been confirmed in two of seven samples of instant coffee by mass spectrometry as well as by liquid chromatography-thermal energy analysis at levels of 1.5 and 2.8 ppb (μg/kg). In one of six samples of roasted, ground coffee, *N*-nitrosopyrrolidine was found at a level of 0.4 ppb (μg/kg) (Sen *et al.*, 1990).