CHAPTER 7

TESTING THE SILICONE RUBBER TRAP ON REAL SAMPLES

7.1. INTRODUCTION

In the previous chapters we have shown, using gas standards, that aldehydes can be derivatised and pre-concentrated on the silicone rubber trap. They are successfully thermally desorbed and analysed by GC - FID or MS. However, it is also important to study the ability of the silicone rubber trap to derivatise and pre-concentrate aldehydes from real life gaseous samples.

In this chapter, the use of the silicone rubber trap is tested on several real samples. These samples were collected from both indoors and outdoors as well as inside cars. These are areas where we usually expect formaldehyde to be present. In addition the headspace of three different beers were sampled for acetaldehyde analysis.

In view of the difficulties experienced with the purity and loading of the derivatising reagent, as well as the method of quantitation used, the results obtained are at best semi-quantitative. These tests serve only to demonstrate the application of *in-situ* derivatisation on silicone rubber traps for real sample analysis.

7.2 EXPERIMENTAL

The traps, used to analyse for HCHO content, were coated with PFBHA headspace from the pure reagent (section 6.3.4) for 10min at a flow rate of 5ml/min. All air samples were collected for 50min, using a GilAir-3 air sampling system from Gilian, set at a collection flow rate of 10ml/min.

The traps, used for the beer analysis, were coated with PFBHA headspace from the pure reagent for 50min at a flow rate of 10ml/min, except the Black Label beer which was loaded for 10min. Acetaldehyde in beer was analysed by collecting the dynamic headspace of approximately 40ml of beer from an impinger type device, similar to that used for the collection of aqueous PFBHA (section 6.3.2). The nozzle of the impinger is above the surface of the beer, which was stirred by a glass coated magnetic stirrer at 500 rpm. The impinger was immersed in a water-ice bath to limit the amount of water condensation in the trap. Nitrogen gas was used to load the headspace of the beer at a flow rate of 10ml/min for 10 minutes. The combination of stirring and nitrogen gas blowing over the beer surface, allowed for minimal foaming of the beer. Hence, no anti-foaming agent was required.

All samples were collected using 2 silicone rubber traps arranged in series connected with a teflon tube. The traps were analysed using the TCT4020 HP GC-FID instruments, with the conditions as described in table 6.1. The temperature programs used are listed in table 7.1 and 7.2.

Ideally gas chromatography with mass spectrometric detection should be used when testing real samples, as overlapping peaks can easily be discerned. Unfortunately, we could not use our quadrupole mass spectrometer at the time, as it was not providing adequate sensitivity.

7.3 RESULTS AND DISCUSSION

Table 7.1 lists the air samples collected and formaldehyde amounts obtained from both traps, calculated as described in section 5.3. The formaldehyde-oxime blank value (peak area) was subtracted from the real sample HCHO-oxime peak areas, before the HCHO amount was calculated. The peak area blank value was calculated by taking the average of a series of PFBHA blanks plus 3 times the standard deviation thereof resulting in a peak area of 67,781 uV.s (i.e. 23.69ng HCHO). The HCHO gaseous concentration in part-per-million (ppm), was calculated by taking the sum of HCHO (ng) in each trap and dividing it by the collection volume. This value was then divided by the conversion factor of 1.23 [6] to convert the HCHO unit of ng/ml to ppm, shown in table 7.1. The percentage trapping efficiency was also determined.

Table 7.2 lists the beer samples collected and acetaldehyde (CH_3CHO) amounts obtained from both traps, calculated as described in section 5.3. The CH_3CHO gaseous concentration in part-per-million (ppm), was calculated by taking the sum of CH_3CHO (ng) in each trap and dividing it by the collection volume. This value was then divided by the conversion factor of 1.8 [6] to convert the CH_3CHO unit of ng/ml to ppm, shown in table 7.2. The percentage trapping efficiency was also determined.

7.3.1 AIR SAMPLES

All air samples collected, listed in table 7.1 are depicted in figures 7.1 to 7.7 for trap 1. Immediately apparent in all of these chromatograms is the repeatable retention times and peak heights of the silicone degradation peaks, indicated with an asterisk (*). In addition, the PFBHA, HCHO-oxime and C12 peaks display consistent retention times throughout.

Figure 7.4 shows a chromatogram of parking lot air sampled using the silicone trap, without any PFBHA loaded on it. Figure 7.3 shows a dramatic decrease in the complexity of the chromatogram obtained, when sampling air from the parking lot using a PFBHA-coated silicone trap. Several peaks have disappeared; we believe this is a result of various carbonyl compounds in the air reacting with the PFBHA. We assume most of the other peaks are hydrocarbons emitted from the car exhausts. As expected, formaldehyde is present in the air, particularly as a result of incomplete combustion of hydrocarbons in fuel.

A problem occurring with the parking lot samples was the extinguishing of the flame on the FID, as seen after 5 min on the chromatogram in figure 7.4. In addition the sensitivity of the instrument was halved after these samples were run. We suspect that fine dust particles may have entered the column, blocking it in the process. The sensitivity was restored by cutting off 30cm of the capillary column.

Figure 7.5, showing the air sampled from a bar, indicates the presence of formaldehyde resulting from tobacco smoke. In addition, alcohol (ethanol) eluting at 2min, and acetaldehyde are also present as expected. Notice, however, that the ratio of the acetaldehyde-oxime peaks are not what we expected, peak 1 should usually be half the size of peak 2. Analysis with an MS would have eliminated this uncertainty.

A comparison of the chromatograms for sampling the indoor air of a new car (figure 7.6) and an old car (figure 7.7) indicate the presence of HCHO in both, with the new car having a much higher amount (table 7.1). Nevertheless, HCHO is present in the older car too, along with other volatiles notably absent from the newer car. This HCHO probably originates from the exhausts of other cars during traffic.

The results obtained in table 7.1 indicate breakthrough onto trap 2, despite PFBHA still being present on trap 1. Consequently, the calculated trapping efficiencies are much lower than expected. This contradicts our breakthrough (section 6.6) and reaction efficiency (section 6.5) studies. From these studies we observed no breakthrough of the HCHO-Oxime after 3 litres of air sampling at a flow rate of 10ml/min. We only sampled 500ml of air. In addition, reaction efficiencies for HCHO and PFBHA were observed to be between 75 and 95%.

Martos and Pawliszyn [22] have suggested that the reaction rate between PFBHA and HCHO is directly proportional to the concentration of HCHO, only while the PFBHA is minimally consumed. Once the reagent is no longer in excess, the reaction rate will decrease.

With this information, we can deduce why breakthrough occurred onto the second trap. The average peak area (plus 3 times the standard deviation) of PFBHA loaded onto the trap for 10min at 5ml/min is 482,562uV.s (n=5). For the data from the newly carpeted laboratory, the peak area of PFBHA remaining on trap 1 is 199,580uV.s. This indicates that 58%, more than half, of the PFBHA has been consumed. The reaction rate between PFBHA and HCHO has therefore decreased and we no longer have the >80% trapping efficiency. Similar trends were observed for the other air samples, except for the indoor air of the new car (trap 1). Here we suspect that the amount of PFBHA loaded onto the trap was more than we expected.

Our tests in the laboratory were based on the reaction between PFBHA and HCHO alone. With the real samples, however, other aldehydes and carbonyl groups are present in the air and will also react with the PFBHA, contributing to its rapid depletion and consequent decreased reaction rate with HCHO. It is therefore necessary to use a back-up trap when collecting the real gaseous samples.

7.3.2 HEADSPACE BEER SAMPLES

Figures 7.8 to 7.11 show the chromatograms obtained by sampling the dynamic headspace of various beers, from trap 1. Once again, the silicone, PFBHA, HCHO-oxime and acetaldehyde-oxime peaks show consistent retention times.
Unfortunately, extinguishing of the flame on the FID was also experienced with these samples, as shown in figure 7.8 at 5 min. A temperature difference of at least 10°C between the beer and the trap, had to be maintained during sampling to avoid condensation of water in the trap and consequent extinguishing of the flame.
Also noted, was a co-elution of a compound from the beer with our internal standard, dodecane (C12). An average peak area of 15,000 uV.s for C12 was used for the calculations (section 5.3). Another peak, at 13.5 min also co-eluted with one of our silicone peaks. If these peaks were of interest to us, the use of a mass spectrometer would be ideal, as the silicone peak can easily be subtracted from the co-eluting peak based on its unique m/z ratios.

It has been suggested that beers not brewed locally have a higher acetaldehyde content, as a result of the ageing process. These beers take longer to reach the public, as they must be transported in, from outside the country first. Windhoek Light, is an example of a lager beer not brewed locally. From table 7.2, it is clear that the amount of acetaldehyde in the Windhoek Light, is nearly twice as much as for the Castle Lager, which is a local brew.
Figure 7.11 shows the comparison of the collection of the dynamic headspace of Castle Lager beer, with and without PFBHA *in-situ* derivatisation. Unlike the parking lot sample, no peaks seem to have disappeared in the derivatisation trap. Several carbonyl compounds are present in beer [17]. However, longer sampling times would be required to derivatise these carbonyls from the headspace of beer.

Similar to the air samples, we again noted a contradiction with the results listed in table 7.2, and our studies performed in section 6.5. In this case, our concerns for the lack of a leak-tight gas standard sampling set-up, is confirmed by the trapping efficiencies we obtained from the beer samples. These ranged from 14% to 60 %, which is above the 4% reaction efficiency for CH_3CHO pure gas standard with PFBHA determined in section 6.5. The amount of PFBHA on trap 2 for the Castle and Windhoek Light lagers, are higher than the amount of PFBHA on trap 1. This is because trap 2 in both cases was coated with PFBHA first. Trap 1 was loaded with PFBHA immediately afterwards. Based on our previous studies on reagent loading, we presume that the reagent vapour pressure was drastically depleted at that time.

As with the air samples, we believe breakthrough occurred because the PFBHA on trap 1 was consumed by more than 10% of the original amount. This lead to a decreased reaction rate between acetaldehyde and PFBHA

In addition, the isomer peak ratios for the acetaldehyde-oximes obtained from the headspace of beer, are not what we expected. From the reaction of PFBHA with our acetaldehyde gas standard in section 6.5, we determined the average ratio of isomer peak 1 to isomer peak 2 to be 50%. The isomer ratios for the acetaldehyde-oxime from Castle Lager, Black Label Beer and Windhoek Light were 35%, 33% and 66% respectively. We imagine that the isomer ratios may be concentration dependant and that it may also be affected by the presence of moisture in the surroundings.

7.4 CONCLUSION

From the results obtained for analysing real gaseous samples using *in-situ* derivatisation on the silicone rubber trap, we can safely say that it is a very promising technique. Loading the reagent and sampling with the portable pump is quick and easy and the actual collections did not have to be supervised.

In addition, the traps were immediately reusable after every analysis and no loss in performance was observed for the traps.

However, the trapping efficiencies for HCHO and CH_3CHO, were contradictory to our expectations based on our studies in the previous chapter. PFBHA is not minimally consumed and the reaction rates with HCHO and CH_3CHO has decreased. Ideal sampling conditions must still be determined.

Table 7.1. Quantitation of collected real samples for formaldehyde (HCHO) analysis.

	trap 1					trap 2							
air samples	t_R (min)	HCHO-oxime peak area (uV.s)	t_R (min)	PFBHA peak area (uV.s)	**HCHO * ng**	t_R (min)	HCHO-oxime peak area (uV.s)	t_R (min)	PFBHA peak area (uV.s)	**HCHO * ng**	HCHO ** (ppm)	temperature program	%trapping efficiency
newly-carpeted laboratory	13.812	108,259	16.283	199,580	**13.39**	13.822	103,590	16.346	463,402	**11.84**	>0.0410	A	11.53
poorly ventilated office	13.91	86,075	16.371	130,121	**6.05**	13.843	20,313	16.278	12,654	below detection limit	>0.0098	A	~
parking lot	no reagent loaded					13.92	138,493	16.405	246,975	**23.39**	>0.0380	A	~
bar with tobacco smoke	13.817	129,436	16.280	113,792	**20.39**	13.82	115,738	16.314	263,611	**15.86**	>0.0589	B	22.22
indoor air of a new car	13.843	130,070	16.363	463,016	**20.60**	13.836	131,729	16.332	281,955	**21.15**	>0.0679	B	~
indoor air of an 11 year old car	13.851	96,150	16.335	190,944	**9.38**	13.844	74,816	16.369	303,590	**2.33**	>0.0190	A	75.20

* Mass of HCHO(ng) calculated by first subtracting HCHO-blank peak area (67781 uV.s) from the HCHO-oxime peak area. Second, this value is divided by the FID-RRF for the HCHO-Oxime relative to C12 (403.125). Third, the value obtained (HCHO-Oxime (ng)) is divided by the molar mass of the HCHO-Oxime (225g/mol) to give the nmol of HCHO. Finally this value is multiplied by the molar mass of HCHO (30g/mol) to give HCHO (ng).

** HCHO (ppm) calculated by taking the sum of HCHO(ng) of trap 1 and trap 2 and dividing by the volume sampled (500ml). This value is then divided by the HCHO conversion factor (1.23). HCHO conversion factor 1ppm=1.23ng/ml [6].

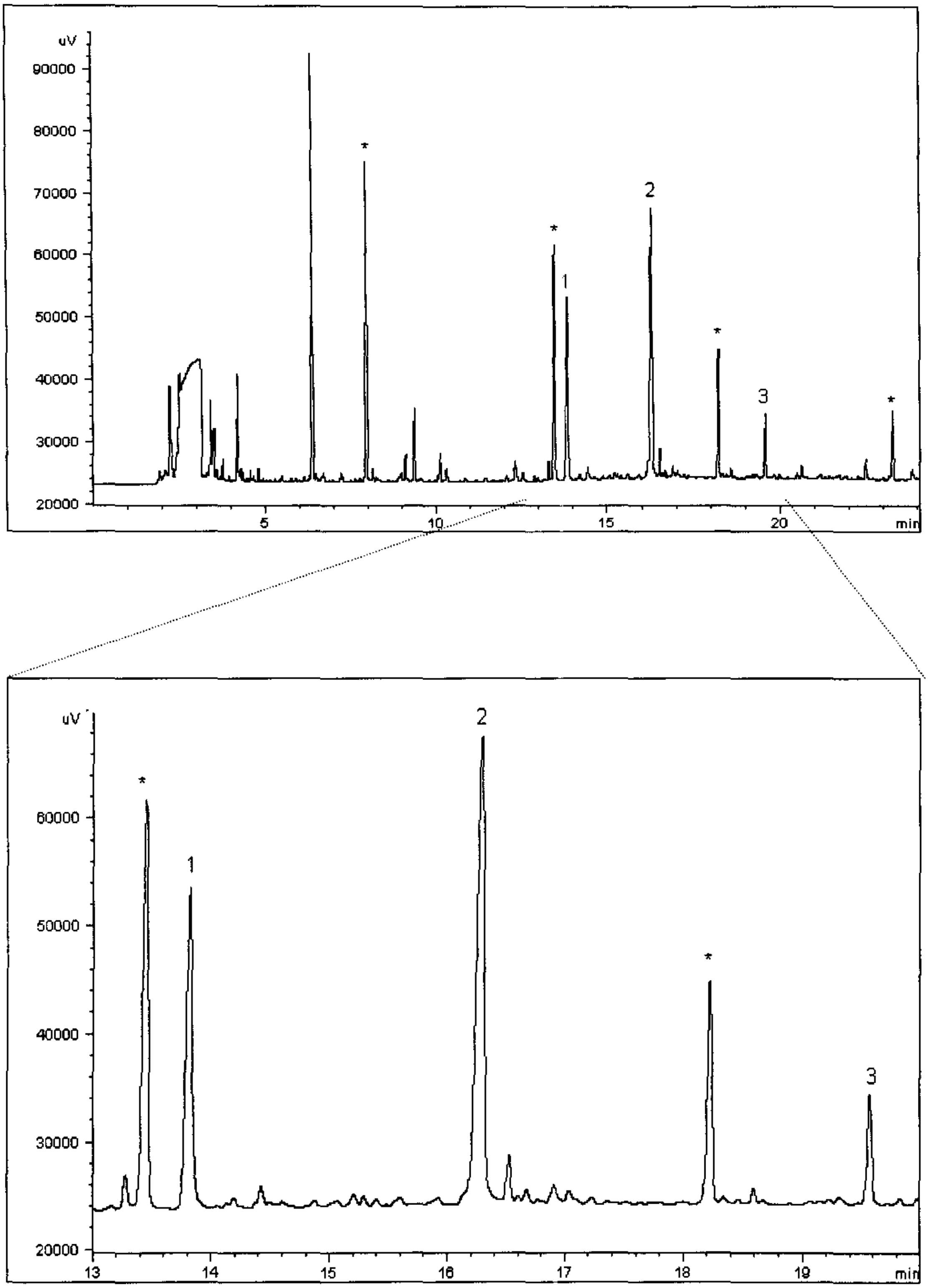
% Trapping efficiency = [1 - (HCHO-trap2/ HCHO-trap1)] x 100

Table 7.2. Quantitation of collected real samples for acetaldehyde (CH_3CHO) analysis .

	trap 1					trap 2					$CH_3CHO^{\#\#}$ (ppm)	temperature program	%trapping efficiency
headspace beer samples	t_R (min)	acetal-oxime peak area (uV.s)	t_R (min)	PFBHA peak area (uV.s)	**$CH_3CHO^{\#}$ ng**	t_R (min)	acetal-oxime peak area (uV.s)	t_R (min)	PFBHA peak area (uV.s)	**$CH_3CHO^{\#}$ ng**			
castle lager	16.767	105,718	16.422	913,378	**160.26**	16.756	82,671	16.334	333,340	**107.96**	>1.4901	B	32.63
	17.044	299,607				17.021	190,382						
black label	16.956	43,909	16.501	38,076	**69.34**	16.935	19,062	16.521	98,901	**28.39**	>0.5429	B	59.06
	17.224	131,469				17.188	52,738						
windhoek light	16.794	242,898	16.429	1,160,526	**241.33**	16.758	180,366	16.285	90,094	**205.61**	>2.4830	B	14.80
	17.054	367,473				17.034	339,661						

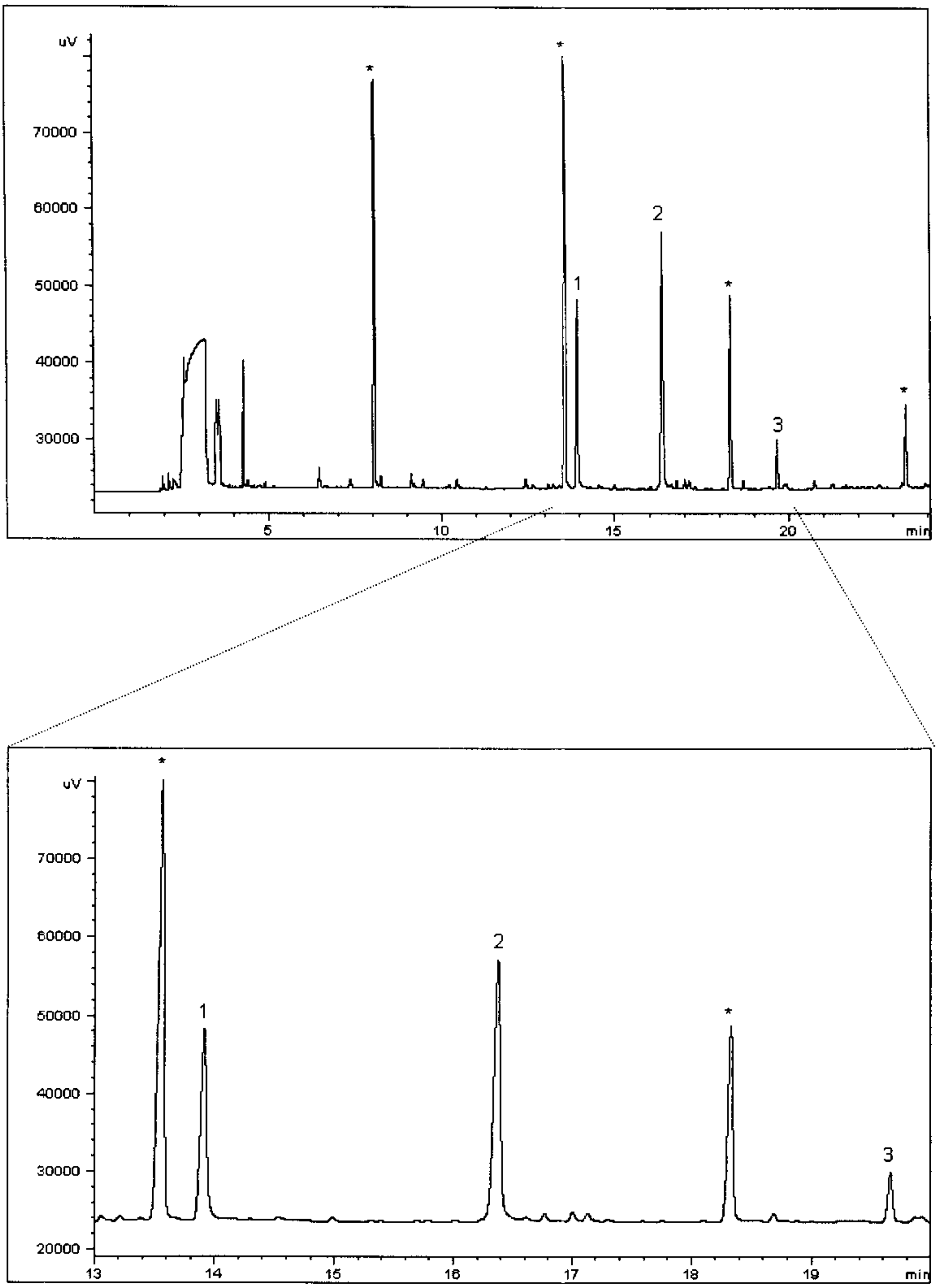
Mass of CH3CHO(ng) calculated by first adding the 2 peak areas obtained for the CH3CHO-oxime. Second this value is divided by the FID-RRF for the CH3CHO-oxime relative to C12 (465.625). Third, this value obtained (CH3CHO-oxime (ng)) is divided by the molar mass of the CH3CHO-oxime (239g/mol) and then multiplied by the molar mass of CH3CHO (44g/mol) to give the mass of CH3CHO(ng).

CH3CHO (ppm) calculated by taking the sum of CH3CHO(ng) of trap 1 and trap 2 and dividing by the volume sampled (100ml). This value is then divided by the conversion factor (1.8). CH3CHO conversion factor 1ppm=1.8ng/ml.



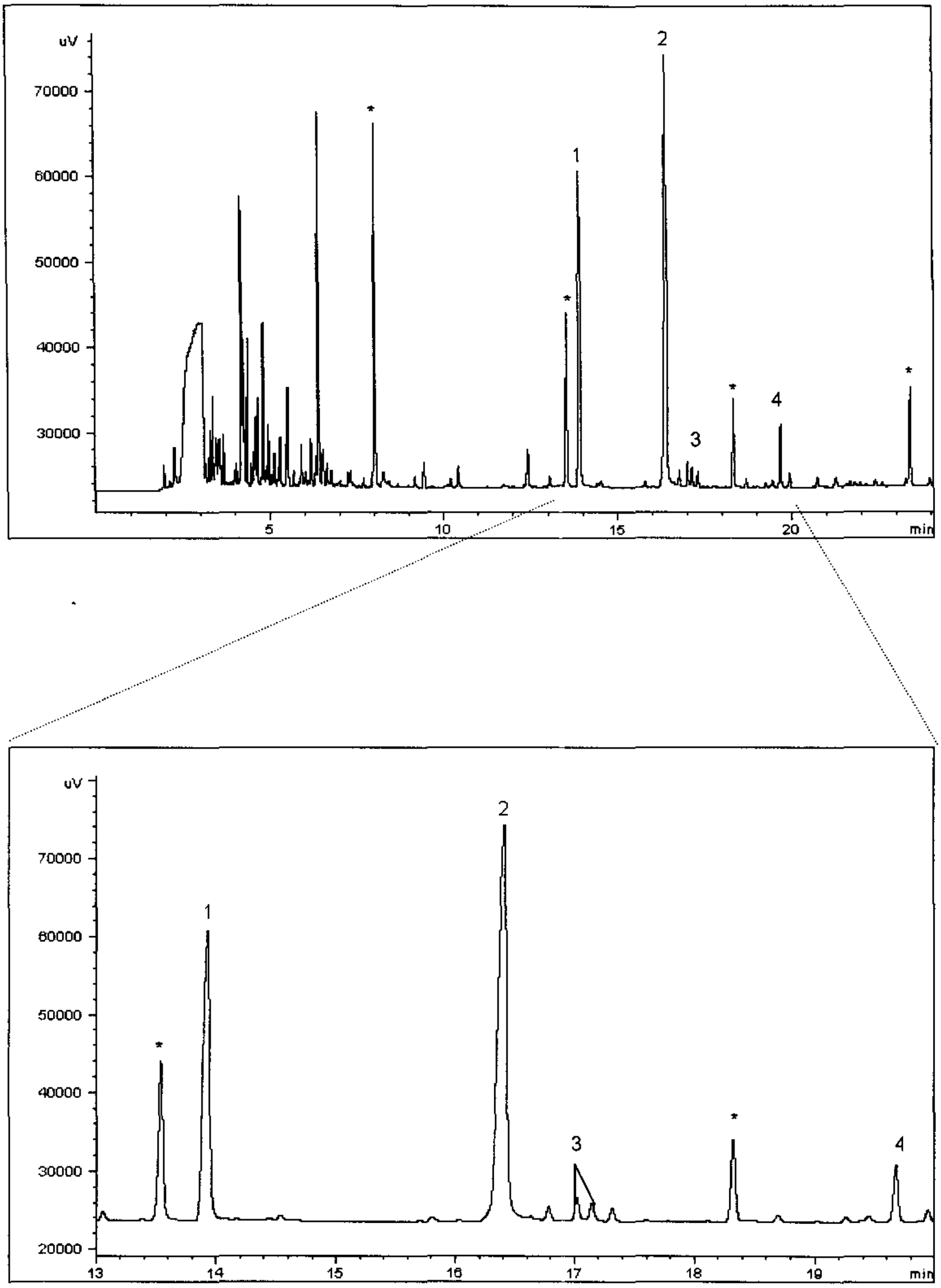
* Silicone degradation peaks	1. HCHO-Oxime
2. PFBHA	3. 20ng C12

Figure 7.1. GC-FID chromatogram of an air sample from a newly-carpeted laboratory.



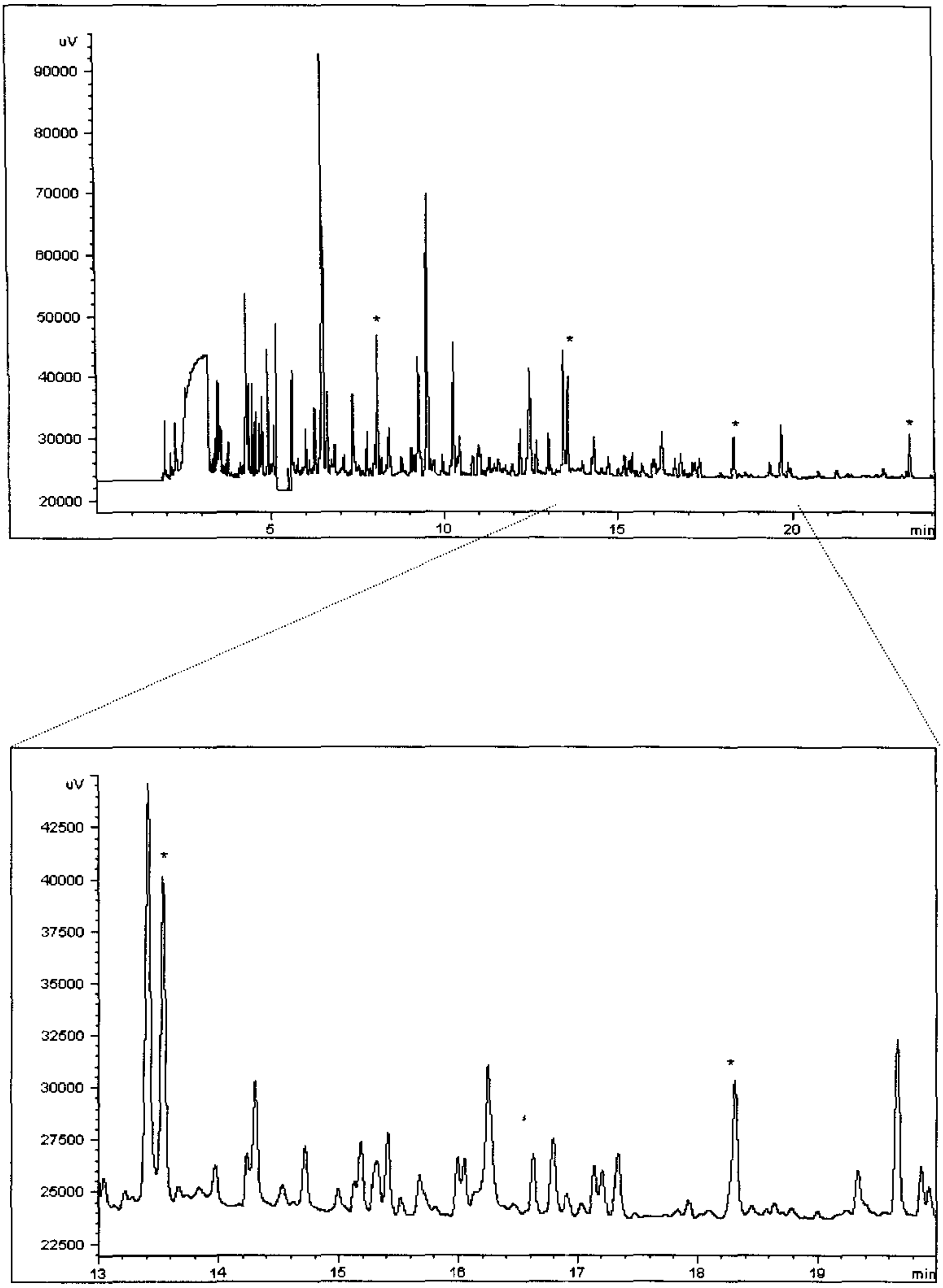
* Silicone degradation peaks
1. HCHO-Oxime
2. PFBHA
3. 20ng C12

Figure 7.2. GC-FID chromatogram of an air sample from a poorly ventilated office.



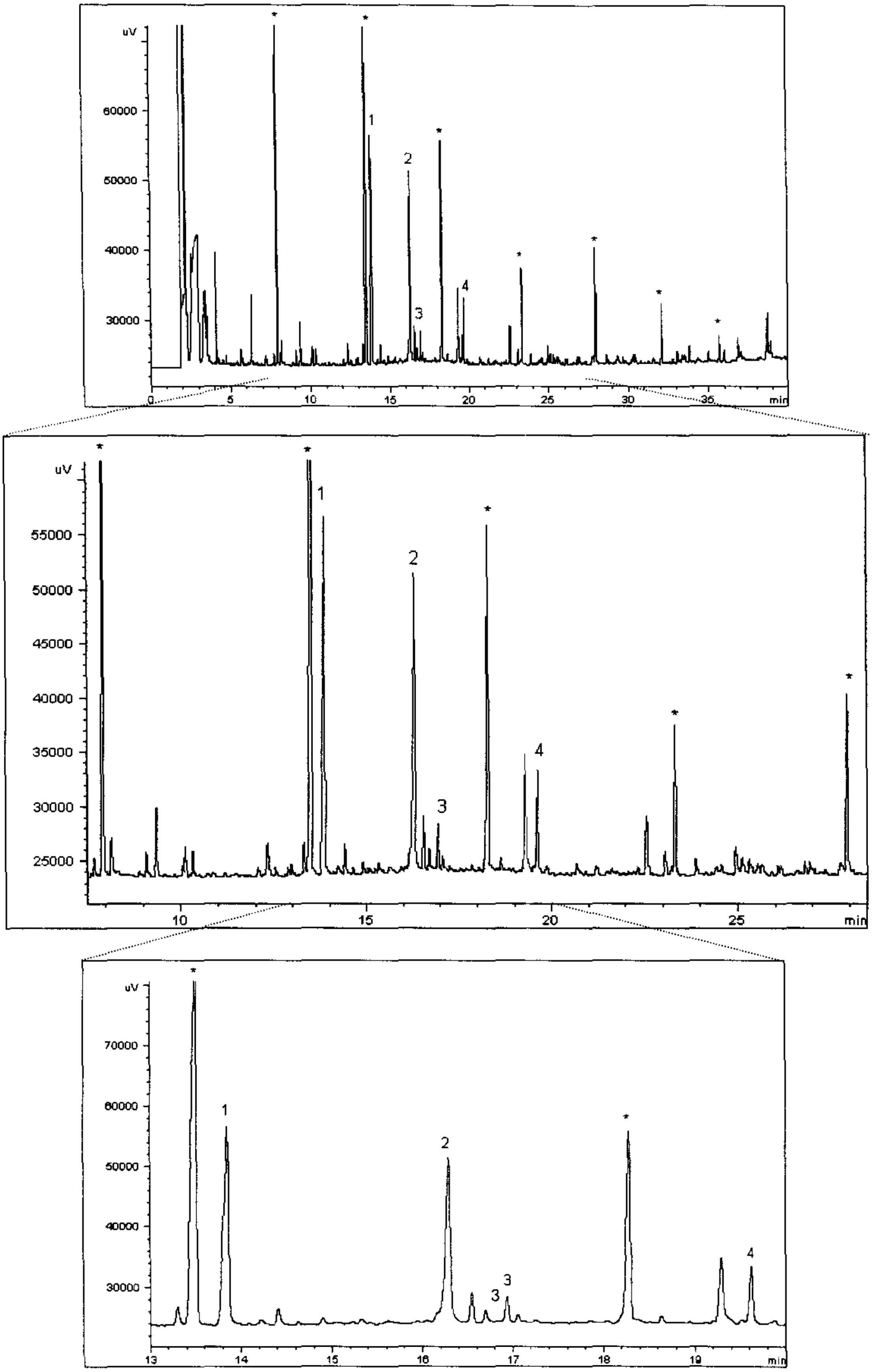
* Silicone degradation peaks 1. HCHO-Oxime
2. PFBHA 3. Acetaldehyde-oxime 4. 20ng C12

Figure 7.3. GC-FID chromatogram of an air sample from a parking lot.



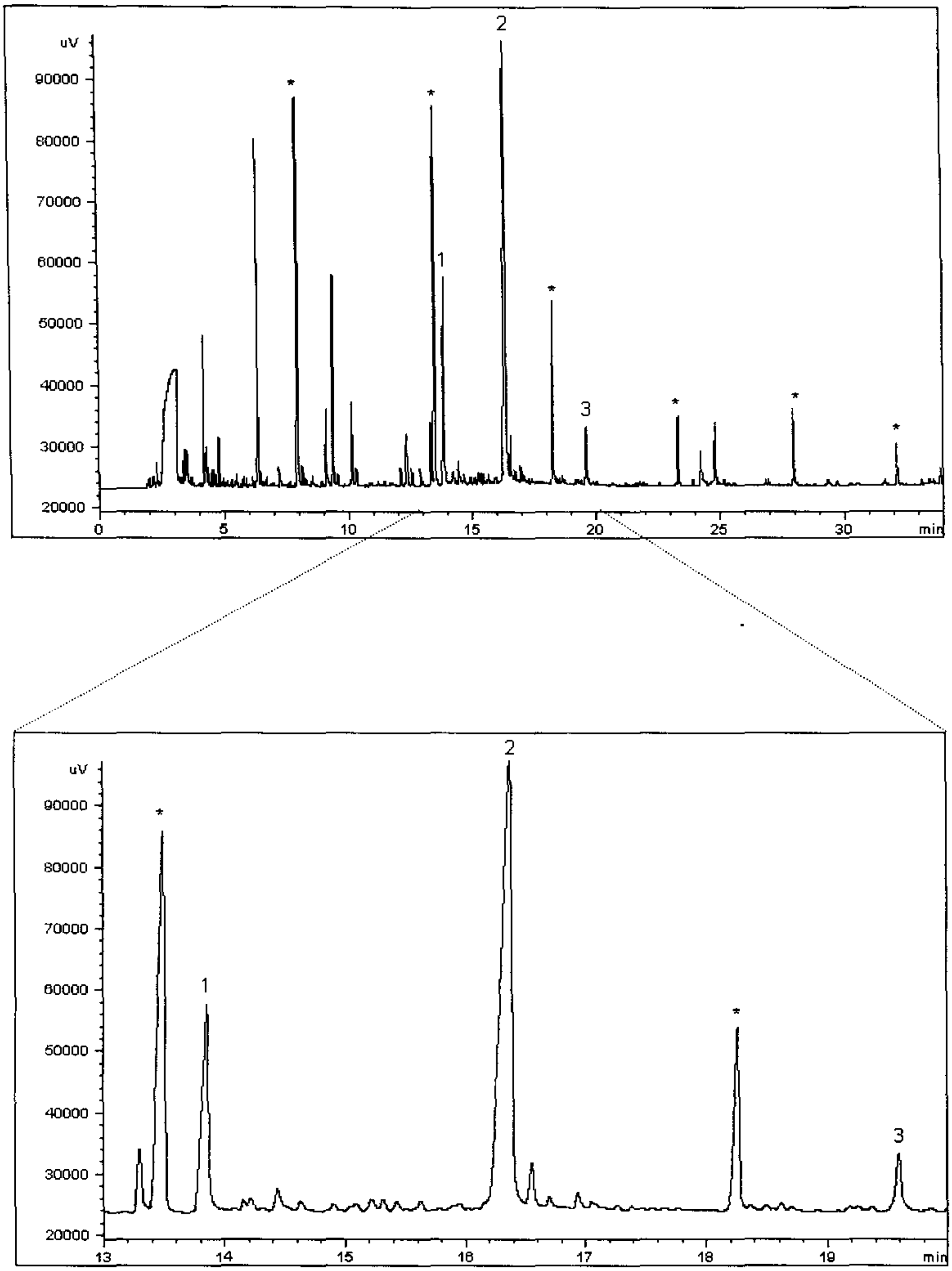
* Silicone degradation peaks

Figure 7.4. GC-FID chromatogram of parking lot air sample without PFBHA in-situ derivatisation.



* Silicone degradation peaks 1. HCHO-Oxime 2. PFBHA
3. Acetaldehyde-Oxime 4. 20ng C12

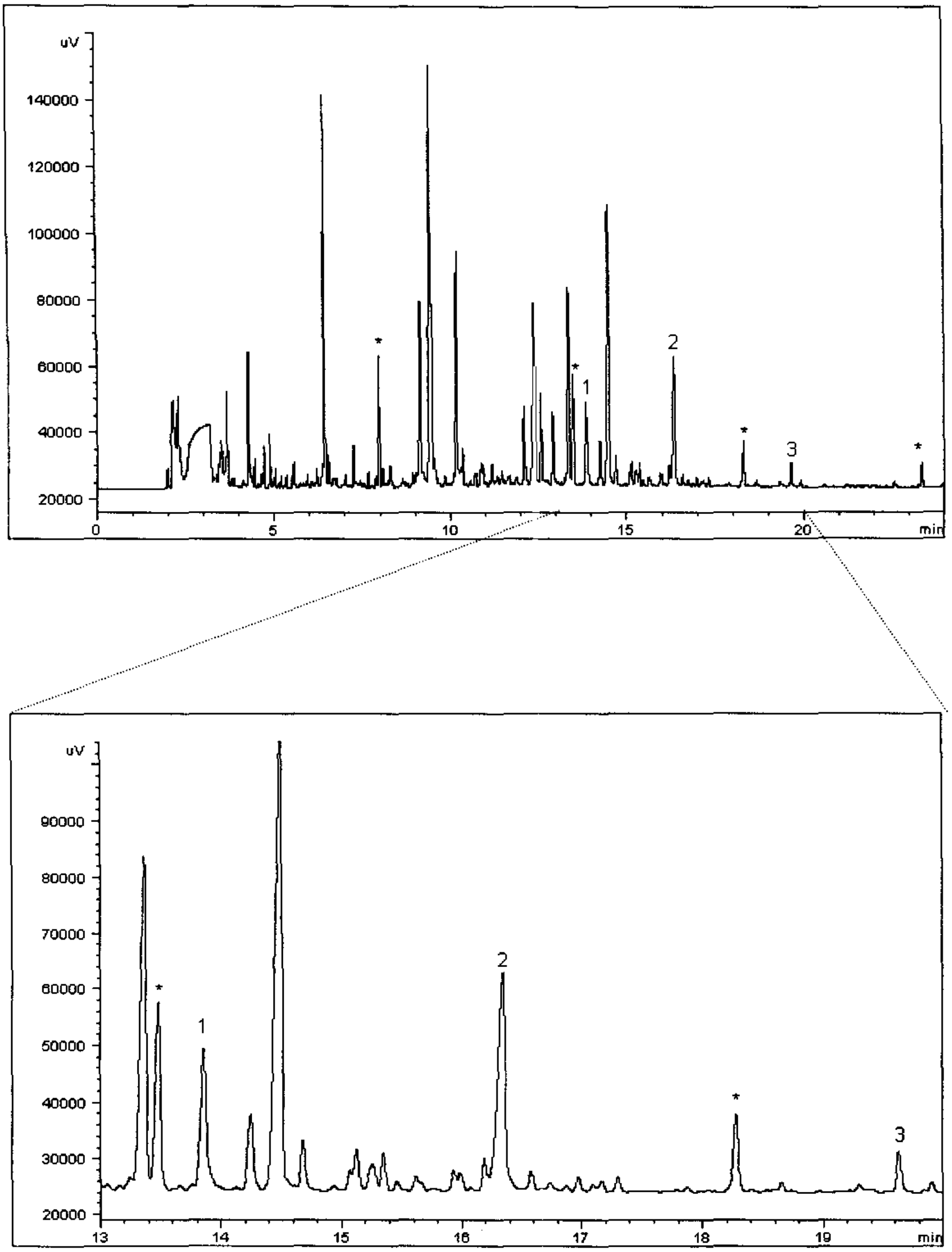
Figure 7.5. GC-FID chromatogram of an air sample from a bar filled with tobacco smoke



* Silicone degradation peaks
2. PFBHA

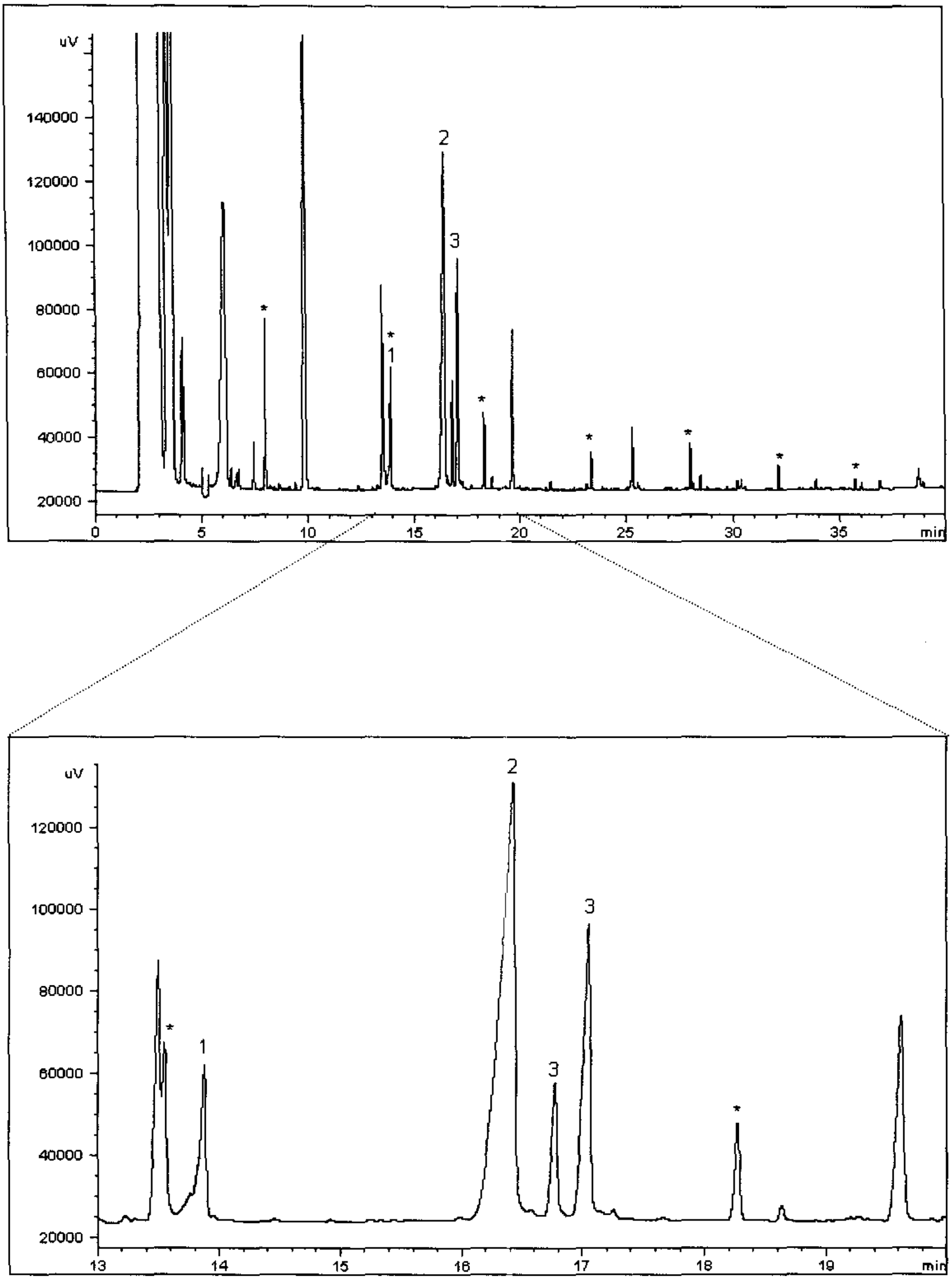
1. HCHO-Oxime
3. 20ng C12

Figure 7.6. GC-FID chromatogram of the indoor air of a new car.



* Silicone degradation peaks 1. HCHO-Oxime
2. PFBHA 3. 20ng C12

Figure 7.7. GC-FID chromatogram of the indoor air of an 11 year old car.



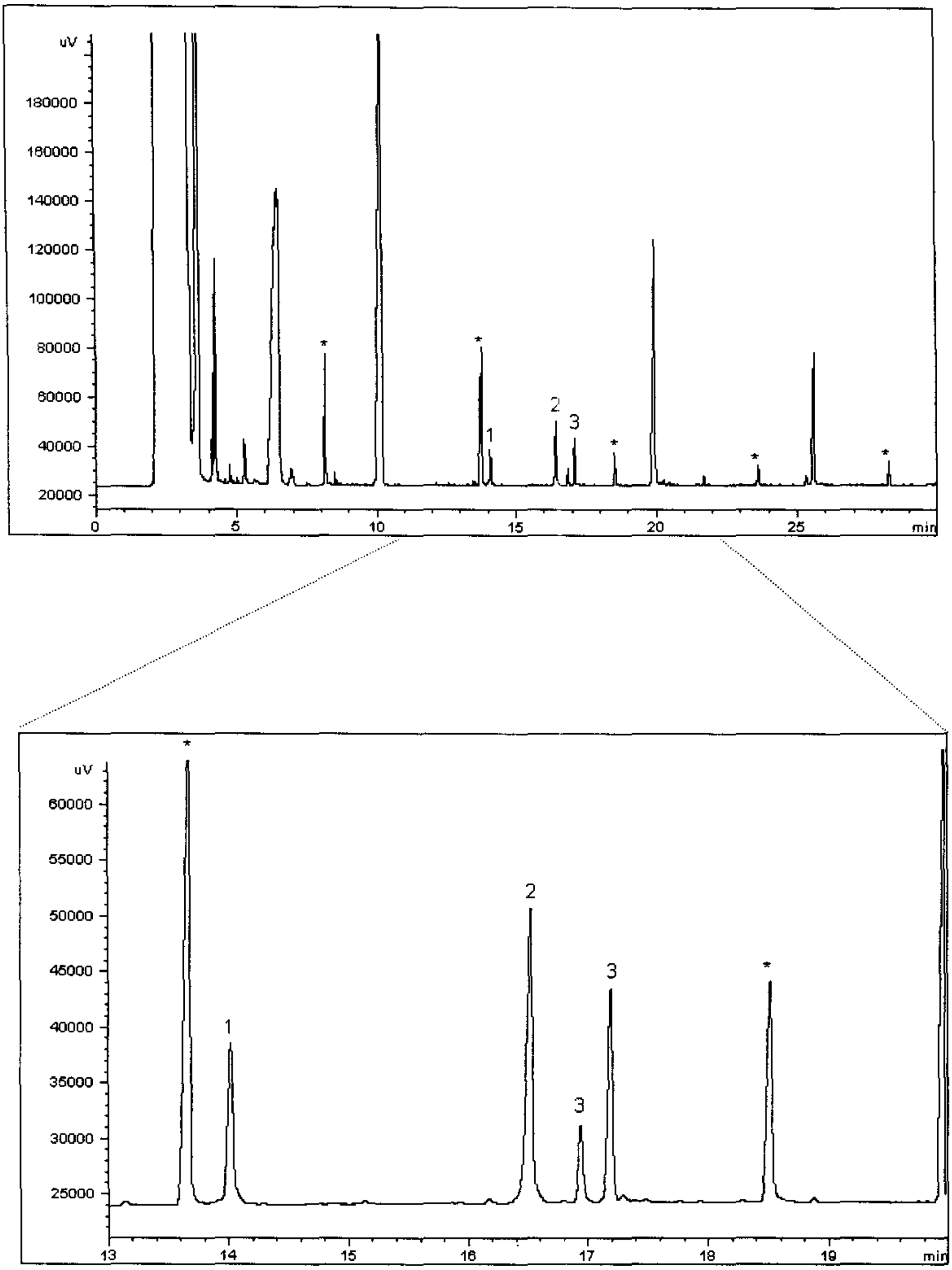
* Silicone degradation peaks

2. PFBHA

1. HCHO-Oxime

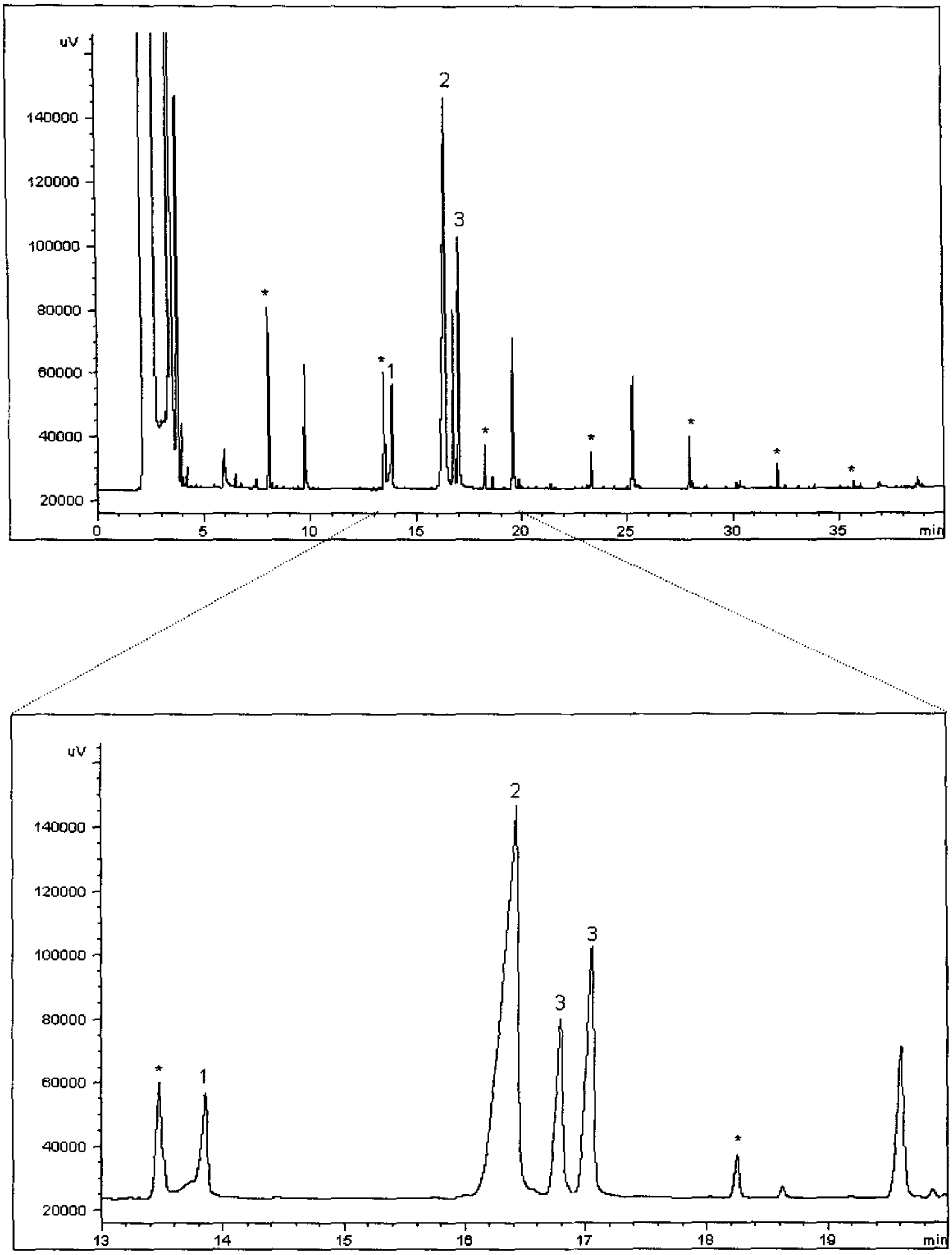
3. Acetaldehyde-Oxime

Figure 7.8. GC-FID chromatogram of Castle Lager headspace sample.



* Silicone degradation peaks 1. HCHO-Oxime
2. PFBHA 3. Acetaldehyde-oxime

Figure 7.9. GC-FID chromatogram of Black Label Beer headspace sample from trap 2.



* Silicone degradation peaks
1. HCHO-Oxime
2. PFBHA
3. Acetaldehyde-oxime

Figure 7.10. GC-FID chromatogram of Windhoek Light beer headspace sample.

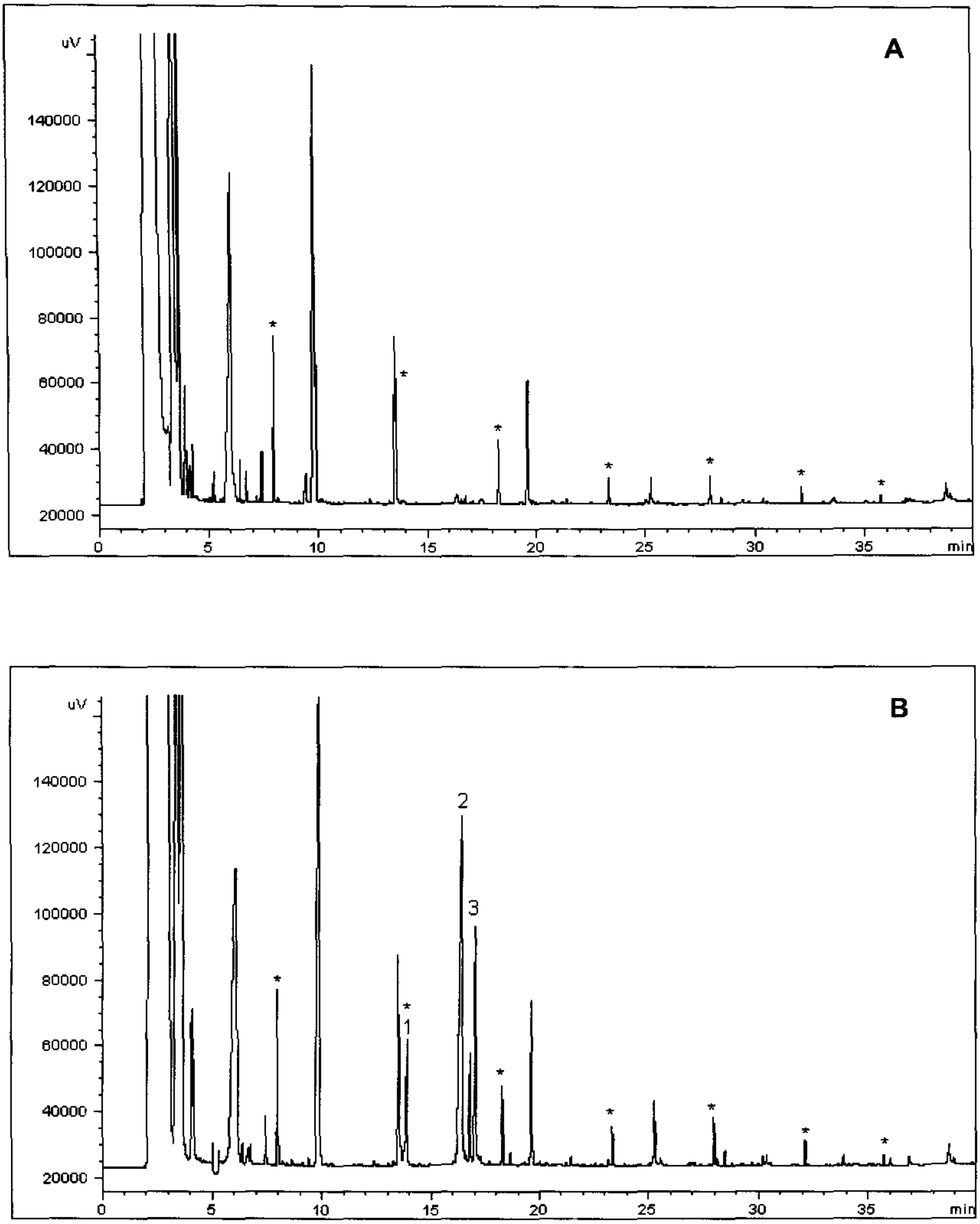


Figure 7.11. **A** GC-FID chromatogram of Castle Lager headspace sample without PFBHA *in-situ* derivatisation.
B GC-FID chromatogram of Castle Lager headspace sample with PFBHA *in-situ* derivatisation (figure 7.8).