QUALITY AND SAFETY OF UNSHELLED WALNUTS

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ABSTRACT

Bleaching procedures for in-shell walnuts were examined in order to minimize or eliminate chloroform. It was found that use of 5% hydrogen peroxide under alkaline conditions gave excellent color with no production of chloroform. Walnuts which were only washed or which were bleached with peroxide or ozone had better flavor after processing than chlorine-(hypochlorite) bleached walnuts.

OBJECTIVES

This project was begun because of concern over the current practice of bleaching in-shell walnuts with chlorine in the form of sodium hypochlorite. The concern came about because of some European importers who detected trace amounts of chloroform in bleached walnuts from the United States. Chlorine is known to react with organic materials to produce chloroform and other chlorinated compounds. A recent article (1) pointed out that many chlorinated organics are suspected carcinogens, and that most users are attempting to phase out use of chlorine. The immediate problem for walnut processors is that several countries are already refusing to accept chlorine-bleached walnuts. Objectives of the project were: 1) to confirm that chloroform is present in walnuts and that it results from chlorine bleaching, and 2) to develop alternate procedures to provide in-shell walnuts that meet appearance standards. Two other goals associated with the objectives were to develop qualitative and quantitative measures of chloroform in walnuts and to devise objective methods to measure color change resulting from bleaching. Finally, it was important to determine whether bleaching methods affected flavor and storage life of the product.

PROCEDURES

As we reported in 1992, the change in color resulting from washing and bleaching was measured with a Minolta Chroma CR200 Color Reflectance Meter. This instrument measures L, a, and b values in which L is a measure of black to white on a scale of 0 to 100 respectively, and a and b are hue values ranging from -100 to +100. Although all three values were taken at each measurement, it was found that values for L, alone, were as good for our purpose as an adjusted combination of all three values. Because of the irregular dimpled surface of walnut shells and the high variability of color even on a single shell, six readings were taken at different locations on each walnut. In experiments a batch of ten walnuts was used and the sixty reflectance readings were averaged. Each batch was then subjected to one or more treatments , and after each treatment sixty readings were again taken in the same way.

At least two ten-walnut batches were subjected to each treatment or sequence of treatments as follows. A total of 24 samples of ten unbleached walnuts were segregated and reflectance readings were taken as described above. They were then divided into three groups of eight 10-nut batches. One group was not washed and the other two were washed with strong scrubbing similar to the action of a commercial mechanical scrubber. One group was washed with a 0.1% solution of a detergent followed by rinsing; the other was washed with water alone. The nuts were dried and reflectance was measured again on all 24 samples. Then each of the unwashed, water-washed and detergent-washed garoups was further divided into four groups of two batches. Each of these groups was bleached by a different procedure: 1) 2.5% sodium hypochlorite for three minutes, 2) 1% sodium hypochlorite for three minutes, 3) 5% hydrogen peroxide at pH 9-10 for three minutes, and 4) saturated ozone at pH 3-4 for ten minutes.

After the final treatment L-reflectance values were measured once more. Thus we obtained average ΔL values for washing and bleaching and for bleaching alone, using two wash methods and four bleaching procedures. Results are summarized in tables I and II.

For sensory evaluation tests we used the same bleaching procedures described above for twenty-pound batches of walnuts which had been water-washed in a Magna Scrubber[R]. The four batches of nuts were air-dried and placed in storage at ambient temperature (68-75°F). For testing, enough nuts were cracked to provide two pounds of nutmeats. The nut kernels were chopped and mixed, and tasted by a panel against unbleached controls. Panelists were presented with a labeled control and two numbered samples, one of which was a duplicate control and the other a bleached sample. They were asked to designate which numbered sample was the same as the control, and to say if either sample had off-flavor. The storage tests are still in progress, so only results of the initial panel tests are reported.

A very sensitive method for detection of chloroform in tree nuts is the technique of gc-ms, gas chromatography combined with mass spectrometry.(2) The technique can be applied to headspace air above a sample of walnuts or walnut shells. A small sample of the air from a closed vessel maintained at constant temperature is removed with a syringe and injected into the chromatograph which emits the sample into the mass spectrometer. The latter acts as a detector by monitoring ions of a specific mass to charge ratio characteristic of chloroform (Figure 1-4). Measuring ion current of the ions of 70, 83, 85, and 87 amu gives a peak which identifies chloroform and which is sensitive at less than 1 ppm. Quantitation of this peak is difficult, and we are still refining procedures.

RESULTS AND CONCLUSIONS

The effects of washing and bleaching walnuts are presented in Tables I and II. Samples of unwashed walnuts have average L-reflectance values of 47.5-49 units. Washing, either with water and detergent or with water alone, produces an increase (improvement) in L-value of 2.5-3 units. Each of the bleaching methods then provides a further increase of 2.5 to 6 units.

Sodium hypochlorite is effective in bleaching shells at 2.5% concentration and almost as good at 1%. Scrubbing before bleaching did not give a statistically significant improvement over bleaching alone. In every case, some chloroform was produced by chlorine bleaching. Use of 5% hydrogen peroxide at a pH of 9-10 was slightly more effective than the chlorine treatments. It consistently provided walnuts with good appearance and no trace of chloroform. A pre-scrub has a slight advantage with peroxide bleaching. Although it was not proven in our limited experiments, the pre-scrub may also conserve peroxide, especially if solid organic matter removed in washing is separated before peroxide treatment. Because iron catalyzes decomposition of peroxide, our experiments were run in glass or plastic vessels. In practice, peroxide bleaching should be done in plastic, enameled or stainless steel equipment. We did not obtain data on rates of peroxide loss; thus cost relative to chlorine bleaching could not be estimated. However, peroxide is almost certain to be more expensive than chlorine treatment.

Ozone had some capability to bleach, but at least in our system, it was not as effective as the other bleach methods. It works best at low pH and is much more effective if the shells are pre-scrubbed. The ozone also required a longer time (10 minutes vs. 3 minutes for the other bleach procedures).

Chloroform analysis (Figs 1-4) showed the presence of this compound in the shells immediately after hypochlorite bleaching, and in the walnut kernels after short storage. There was no chloroform present in samples which were scrubbed and/or bleached with peroxide or ozone.

Taste panel tests of stored bleached walnuts are still in progress. The initial results from the taste panel within one week after bleaching were interesting, however. A panel of twenty individuals making forty evaluations of each treatment was able to differentiate chlorine-bleached samples from unbleached controls at the one percent probability level. They not only were able to discriminate, but they made a number of adverse comments concerning the flavor of the chlorine-bleached samples, at both levels of bleach concentration (Table III). The same panel was unable to differentiate the peroxide- and ozone-bleached walnuts from controls.

At this point, unless we find some dramatic difference in storage life of products, we recommend that water washing with scrubbing is the safest treatment for unshelled walnuts. Since the effect of bleaching is mainly cosmetic, this would eliminate any possibility of by-products from chemical bleaching. If the preliminary taste panel results hold during storage it may also produce a benefit in walnuts with better flavor. Peroxide seems to be the best alternative if bleaching must be done to meet appearance standards. Switching to peroxide will necessitate some alterations in equipment and procedures, and will probably be more expensive.

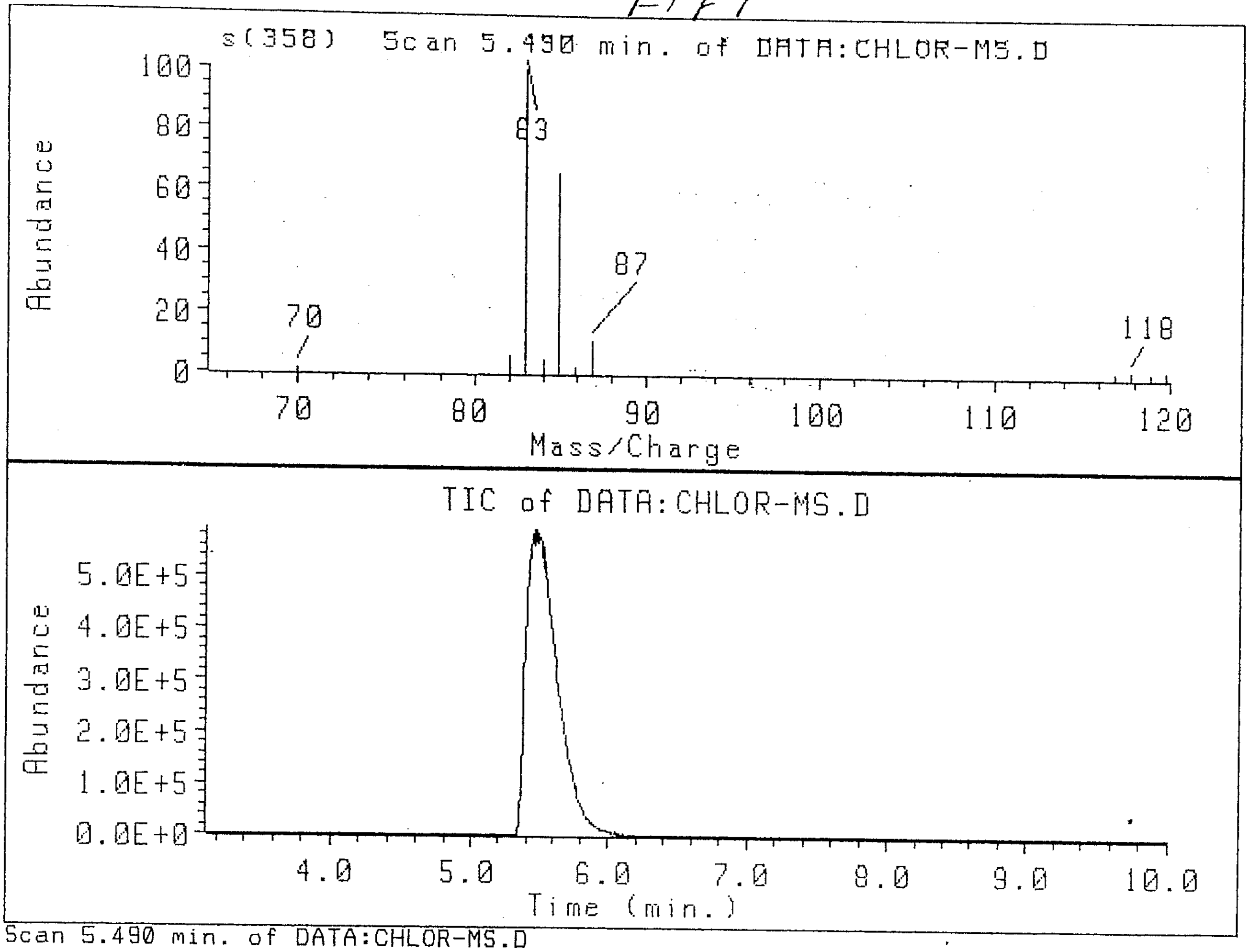
REFERENCES

1. Hileman, B., (1993) Chem and Eng. News, April 19, 11-20.

2. Applied Spectroscopy Reviews (1975) 10 (1) 51-116.

Figures

Frt 1



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AMU.	Abundance	AMU.	Abundance	AMU.	Abundance
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82.05	5.62	85.95	1.49	118.95	1.00
82.95	100.00	86.95	10.28	119.85	1.47
84.05	4.47	116.95	1.17		

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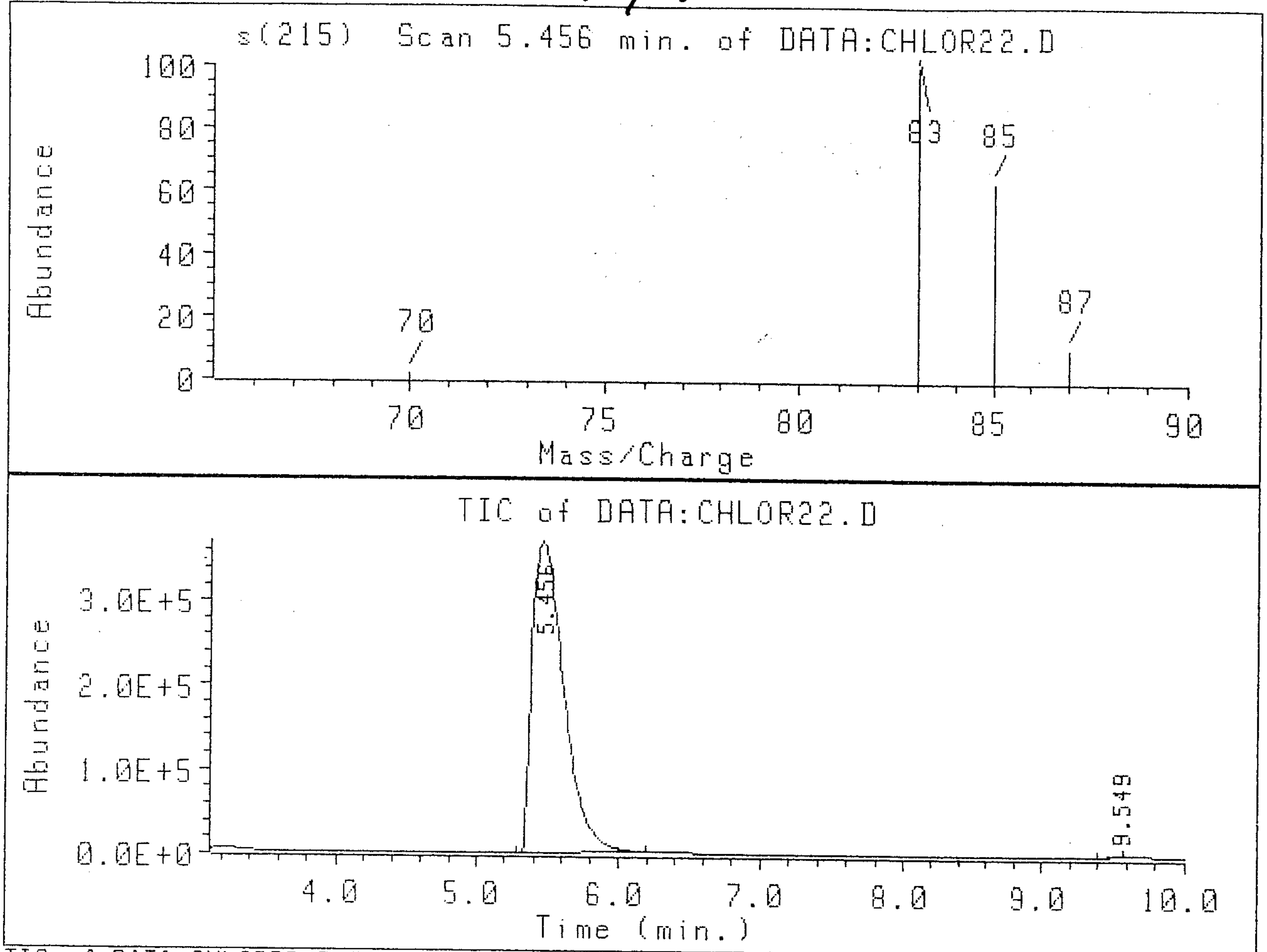
File type: GC / MS DATA FILE

Sample Name: FULL SPECTRA CHLOROFORM 400+EM 50 AMU @ ABOVE

Fig 2



TIC of DATA:CHLOR22.D 2 integration peaks found. Page 1

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2	9.549	BV	0.061	15747	9.390	9.569

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AMU.	Abundance	AMU.	Abundance	AMU.	Abundance
70.00	1.78	85.00	62.91		
83.00	100.00	87.00	10.08		

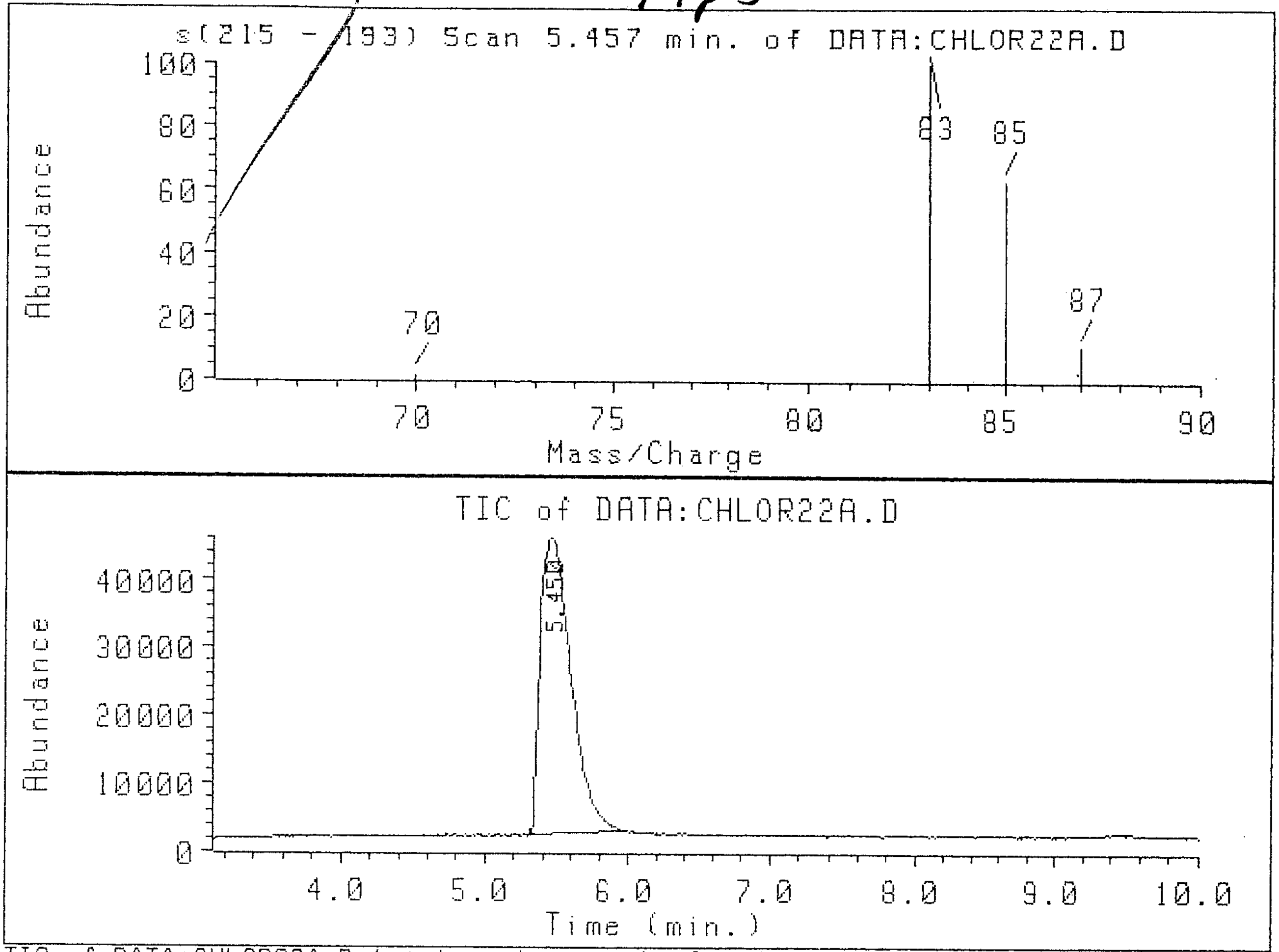
Data file: DATA:CHLOR22.D
File type: GC / MS DATA FILE

Sample Name: PH 11.6 SHELLS 400+EM 100 DEG HEAT 15 MIN
Misc Info:
Operator : STAFFORD

Date : 9 Sep 92 11:31 am
Instrument: MS_5970
Inlet : GC

Sequence index : 0
Als bottle num : 0
Replicate num : 1

Fig 3



TIC of DATA:CHLOR22A.D 1 integration peaks found. Page 1

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
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Scan 5.457 min. of DATA:CHLOR22A.D

AMU.	Abundance	AMU.	Abundance	AMU.	Abundance
70.00	1.37	85.00	62.89		
83.00	100.00	87.00	10.28		

Data file: DATA:CHLOR22A.D
File type: GC / MS DATA FILE

Sample Name: PH 11.6 MEATS 400+EM 100 DEG HEAT 15 MIN
Misc Info:
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Instrument: MS_5970
Inlet : GC

Sequence index : 0
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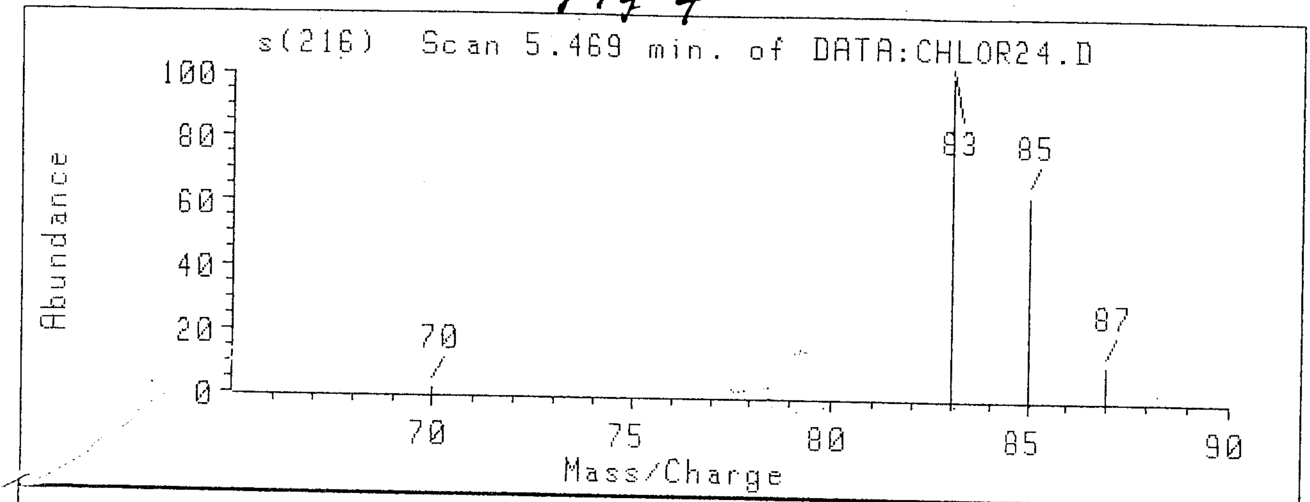
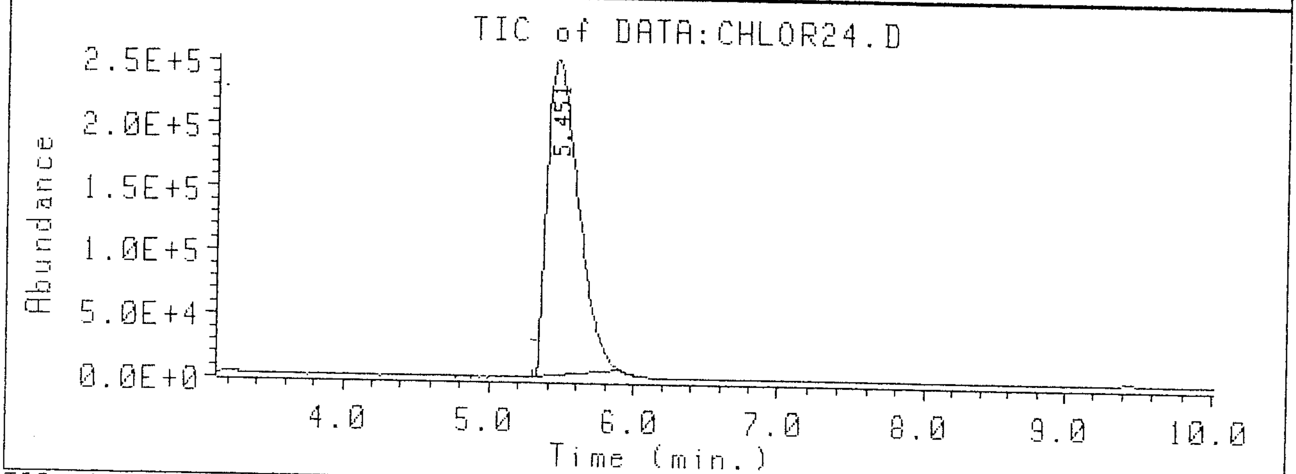
Replicate num : 1

Fig 4





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Page 1

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Scan 5.469 min. of DATA:CHLOR24.D

AMU.	Abundance	AMU.	Abundance	AMU.	Abundance
70.00	1.64	85.00	62.93		
83.00	100.00	87.00	10.20		

Data file: DATA:CHLOR24.D
File type: GC / MS DATA FILE

Sample Name: PH 7 SHELLS 400+EM 100 DEG HEAT 15 MIN SIM 4 IONS
Misc Info:
Operator : STAFFORD

Date : 9 Sep 92 3:28 pm
Instrument: MS_5970
Inlet : GC

Sequence index : 0
Als bottle num : 0
Replicate num : 1

TABLE I

EFFECT OF WASHING UNSHELLED WALNUTS*

Sample	L	SD	a	SD	b	SD
Unwashed	48.93	0.54	+11.56	0.31	+23.41	0.81
Water-washed	51.62	0.45	+12.34	0.41	+25.58	0.78
Unwashed	48.74	1.00	+11.64	0.22	+23.54	0.64
Detergent-wash	51.95	0.93	+12.53	0.32	+25.41	0.51

*Each experiment represents six 10-nut batches of walnuts before and after scrubbing with brushes, using water or 1% detergent solution.

TABLE II

SCRUBBING AND BLEACHING OF UNSHELLED WALNUTS

Sample	Unwashed	Washed		Bleached		Total
L	L	L	ΔL	L	ΔL	ΔL
NaOCl, 2.5%						
Water-wash	49.12	51.47	2.35	56.48	5.01	7.36
	49.28	51.98	2.70	56.43	4.45	7.15
Detergent-wash	48.14	51.12	2.98	55.94	4.82	7.80
	47.80	50.87	3.07	54.94	4.07	7.14
Unwashed	47.68			54.33	6.65	6.65
	47.83			55.91	8.08	8.08
NaOCl, 1%						
Water-wash	48.63	51.45	2.82	55.81	4.36	7.18
	48.53	51.64	3.11	55.12	3.48	6.59
Detergent-wash	47.79	51.41	3.62	54.40	2.99	6.61
	48.82	51.81	2.99	56.04	4.23	7.22
Unwashed	48.41			53.79	5.38	5.38
	47.71			55.68	7.97	7.97
Peroxide, pH9						
Water-wash	48.95	51.53	2.58	57.93	6.40	8.98
	48.59	51.31	2.72	57.91	6.60	9.32
Detergent-wash	49.94	52.92	2.98	59.09	6.17	9.15
	50.41	53.37	2.96	59.35	5.98	8.94
Unwashed	48.88			54.47	5.59	5.59
	48.72			57.32	8.60	8.60
Ozone, pH 3-4						
Water-wash	50.01	52.51	2.50	55.67	2.56	5.06
	48.35	51.06	2.71	53.70	2.64	5.35
Detergent-wash	49.00	52.71	3.71	55.93	3.22	6.93
	47.98	51.37	3.39	54.30	2.93	6.32
Unwashed	47.74			52.04	4.30	4.30
	48.76			52.58	3.81	3.81

Table III

TASTE PANEL TESTS*

Treatment	No. of Evaluations	No. correct	Remarks
2.5% NaOCl	38	28	20 found off-flavor in treated sample. Significant at 1%
1% NaOCl	40	32	23 found off-flavor in treated sample. Significant at 0.1%
5% Hydrogen peroxide	40	22	2 found control off-flavor. 2 found bleached off-flavor. No significant difference.
Ozone	40	14	Remarks indicated no difference. No adverse comments.

*Panel was asked to indicate which of two samples was a duplicate of control.