Volatile Constituents of Southernpea Seed [*Vigna unguiculata* (L.) Walp.]

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Thirty-two samples of southernpea seed [*Vigna unguiculata* (L.) Walp., subsp. *unguiculata*] from commercial and experimental cultivars were analyzed for volatile constituents. Low concentrations of potential toxicants were found in all samples. Sixteen other constituents were also identified and determined semiquantitatively. No relation was found between concentration of any volatile and any known genetic or cultural variable. A novel gas chromatographic (GC)–data system (DS)-controlled mass spectrometric (MS) technique for the analysis of foods and feeds for volatile potential toxicants is described.

It is important to establish the levels of potentially toxic volatiles found naturally in different classes of foodstuffs. Although southernpeas [*Vigna unguiculata* (L.) Walp., subsp. *unguiculata*] such as blackeyed peas, crowder peas, and cream peas are a major food item in the southern states, little is known about their composition. In particular, there is little data on minor components such as volatile compounds and known toxicants.

A few years ago a new, direct unconventional GC technique was developed (Dupuy et al., 1971) for detecting volatiles in flavor work. Recently this technique, commonly called the Dupuy direct transfer system, was improved by interfacing the gas chromatograph with a mass spectrometer and a data system (Fore et al., 1978). This new GS–MS–DS technique was used to determine the nature of the volatiles that are present in southernpeas.

MATERIALS AND METHODS

Materials. Named varieties of seed (Table I) were supplied by the U.S. Vegetable Breeding Laboratory, SEA, U.S. Department of Agriculture, Charleston, S.C. Commercial types were purchased locally in New Orleans.

Standards were research grade chemicals from reliable sources used without further purification. The column packings of poly-*m*-phenoxylene (Poly-MPE, Applied Science Laboratories, State College, Pa.) on Tenax-GC (Tek Lab, Inc., Baton Rouge, La.) were prepared in the usual way (Novotny et al., 1975).

Semiquantitative Analysis. The GC analyses were carried out with a Hewlett-Packard 5700 gas chromatograph with hydrogen flame detector. The injection port was bored to accomodate a 6 mm o.d. × 65 mm glass sample tube. The column was 6 ft × $^1/_8$ in. o.d. stainless steel, packed with 60/80 mesh Tenax GC coated with about 6% poly-MPE. The carrier gas was nitrogen at 20 mL/min.

Samples of seed were ground to a fine powder in a mortar, weighed into a borosilicate glass tube sample holder plugged with glass wool, and inserted into the modified injection port of the gas chromatograph. With the sample tube in place, the carrier gas flow was diverted through the sample tube by a silicone O-ring seal at the bottom and a slotted $^1/_4$ in. o.d. stainless steel ring that projected about 0.5 mm at the top. The regular silicone septum provided enough pressure to seat the tube on the O-ring. The sample was heated to 130 °C and the volatiles were swept onto the cool column (25 °C) for 10 min by the carrier gas. The sample was then removed from the injection port, the system closed, and the column warmed to 40 °C, held for 2 min, then temperature-programmed to 190 °C at 4 °C/min, and finally held at 190 °C for 30 min. After the peaks were identified by mass spectrometry, GC runs were made on samples to which known amounts of the standards were added. The additional height of each peak was used to calculate the change in peak height in parts per billion of standard in a 0.3000-g sample run under uniform conditions. Twenty-seven standards were run in a semiquantitative manner so that from the peak heights maximum values could be assigned for these compounds in the seeds (see Table II).

Qualitative Analysis. The GC–MS–DS system used for identification of GC peaks consisted of a Tracor 222 gas chromatograph interfaced to a Hewlett-Packard 5930A mass spectrometer via a silicone membrane separator housed in the GC oven and an Incos 2000 data system. The GC column was Tenax-GC-poly-MPE, 8 ft × $^1/_8$ in. stainless steel. The carrier gas was helium at 30 mL/min. Ionization voltage was 70 eV.

To eliminate excess water, the volatiles were eluted from 1.2 g of ground seed at 120 °C for 30 min, collected on 0.4 g of Porapak P (Legendre et al., 1978b), and then eluted from the Porapak P to the cool GC–MS–DS column at an inlet temperature of 170 °C for 20 min. After transfer of volatiles, the column was heated rapidly to 80 °C and then programmed to 210 °C at 4 °C/min. The MS–DS was operated in the normal scan mode with 4.5-s scans of a 21-300 amu range. Compounds were identified by comparing their spectra with published spectra (American Society for Testing and Material, 1969). When necessary, raw spectra were processed to eliminate background and overlapping peaks.

Quantitative Analysis. For quantification, the GC–MS–DS system used for qualitative analysis was operated in the multiple-ion detection mode (MID), and different sample preparation, volatiles transfer, and GC parameters were used. To get quantitative transfer of volatiles from the sample to the column, the gas chromatograph was modified by addition of the device shown in Figure 1. This consists of a uniformly heated inlet assembly (Legendre and Dupuy, 1978a) and a condenser assembly which removes water coming from the sample before it reaches the column. Various empty and packed condensers were evaluated in a prototype GC system. The Dupuy direct transfer system of a separate Tracor gas chromatograph (Fore et al., 1972) was modified by attaching an open, thin-walled $^1/_4$ in. o.d. × 4 in. tube between the inlet and the column. The O-ring at the bottom of the injection port was replaced with a Teflon disc that fitted loosely in the injection port but tightly around a $^3/_{16}$ in. × 4 in. tube, which served as a condenser and could be removed through

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Table I. Southern Varieties

sample no.	type	variety	year grown	place	resistant
1	pinkeye	pinkeye purple hull	1975-76	greenhouse	
2	pinkeye	pinkeye purple hull	1976	greenhouse	
3	pinkeye	coronet	1976	greenhouse	
4	whippoorwill	groit	1976	greenhouse	
5	red seed	Chinese red	1976	greenhouse	
6	cream	white acre	1976	field	
7	cream	white acre	1976	greenhouse	
8	cream	Louisiana purchase	1976	greenhouse	
9	cream	Floricream	1976	greenhouse	
10	cream	CR 22-2-21	1976	greenhouse	CCR[a]
11	cream	CR 18-13-1	1976	field	CCR[a]
12	cream	zipper cream	1975	greenhouse	
13	cream	snapea	1976	greenhouse	
14	cream	Ala 963.8	1976	greenhouse	CCR[a]
15	cream	Arlington	1976	greenhouse	
16	large cream	Big boy	1976	greenhouse	
17	cream	CR 17-1-13	1976	field	CCR[a]
18	unknown	field peas (center cut) commercial	1976[b]	field	
19	unknown	field peas (center cut) commercial	1977[b]	field	
20	crowder	Mississippi purple	1975	greenhouse	
21	crowder	knuckle purple hull	1976	field	
22	crowder	brown crowder	1976	greenhouse	
23	crowder	Mississippi silver	1976	field	
24	crowder	Mississippi silver	1976	greenhouse	
25	crowder	crowders (center cut) commercial	1976[b]	field	
26	crowder	crowders (center cut) commercial	1977[b]	field	
27	blackeye	California blackeye no. 5	1974	field	
28	blackeye	grant blackeye-bean	1976	greenhouse	
29	blackeye	magnolia blackeye	1976	greenhouse	
30	blackeye	extra early blackeye	1975	greenhouse	
31	blackeye	blackeye (center cut) commercial	1976[b]	field	
32	blackeye	blackeye (center cut) commercial	1977[b]	field	

[a] CCR, cowpea curculio resistant. [b] Year purchased at local grocery store.

Table II. Compounds Identified in Southernpeas by GC-MS and Quantitated by Gas Chromatography

peak no.	component	min, ppb	max, ppb	mean, ppb	median, ppb	SD,[a] ppb	Cv[b]
1	methanol	1200	7800	2960	2200	1850	0.62
2	acetaldehyde	700	4600	2290	2100	1070	0.47
3	ethanol	550	7300	2450	1300	2100	0.85
4	acetonitrile	250	850	472	460	142	0.30
5	2-propanol[c]	400	2200	1010	900	500	0.50
6	acetone[d]	390	2200	1010	900	430	0.42
7	1-propanol[e]	40	390	131	110	77	0.59
8	methylpropanal	29	190	104	100	39	0.38
9	2-butanol[f]	40	160	72	61	28	0.39
10	2-butanone	74	390	151	120	80	0.50
11	2-methylpropanol	14	240	75	66	60	0.80
12	1-butanol	0	130	17	8	27	1.61
13	methylbutanal[g]	96	430	220	200	78	0.36
14	2-pentanone[h]	31	650	109	90	106	0.98
15	1-pentanol	7	540	53	21	99	1.01
16	toluene	10	200	45	20	58	1.27
17	hexanal	39	350	157	140	76	0.48
18	1-hexanol	4.5	162	37	22	40	1.10
19	ethylbenzene	3	169	19	9	31	1.68
20	*o*-xylene	5	49	12	10	8	0.69
21	styrene[i]	0	18	5.6	5.3	3.4	0.61
22	benzaldehyde[j]	15	200	68	45	60	0.89
23	dodecane	8	72	27	20	17	0.62
24	phenylacetaldehyde	10	190	84	90	59	0.71
25	acetophenone	0	720	46	91	132	2.88
26	naphthalene	1	9	2.7	2.8	1.6	0.60
27	methylnaphthalene	4	150	14	7	27	1.86

[a] Standard deviation. [b] Coefficient of variation (SD/mean). [c] Diethyl ether also identified in this peak. [d] Dimethyl sulfide and carbon disulfide also present. [e] Methyl acetate also present. [f] Chloroform also present. [g] Benzene also present. [h] Pentanal may also be present. [i] Cumene also present. [j] Dichlorobenzene also present.

the injection port when the sample was withdrawn. Evaluations were based on loss of weight from the sample, gain in weight of the condenser, and amount of volatiles found with and without the condenser in the system. A condenser packed with ca. 0.1 g of anhydrous sodium sulfate on 0.2 g of Gas-Chrom P was selected for use with the GC–MS–DS system.

The samples to be analyzed were ground in a Wiley mill with a 30-mesh screen. One gram of ground seed was "sandwiched" between two plugs of volatile-free glass wool in a $^3/_8$ in. o.d. by $3^3/_8$ in. long borosilicate glass tube. The tube was then inserted into an external injection system mounted on the gas chromatograph (Legendre and Dupuy, 1978a). The pipe cap of the inlet was hand-tightened,

Table III. Calibration for Potential Toxicants

compound	slope, ppb/count	Y intercept, ppb	correlation coefficient	range,[a] ppb
acetonitrile (ACNL)	0.009 61	13.0	0.998	48-970
dimethyl sulfide (DMSD)	0.001 83	6.5	0.998	8-677
carbon disulfide (CDSD)	0.000 118	1.1	0.986	0.6-98
chloroform (CHLR)	0.000 258	5.3	0.986	29-98
carbontetrachloride (CTET)	0.001 02	32.0	0.998	30-934
benzene (BNZN)	0.000 145	0.5	0.9997	0.7-81
toluene (TOLN)	0.000 074 2	1.4	0.996	0.6-98
dichlorobenzene (DCBZ)	0.000 132	1.4	0.999	0.6-98
trichlorobenzene (TCBZ)	0.000 217	2.4	0.998	0.7-111
naphthalene (NAPH)	0.000 041 0	0.7	0.9988	0.6-98
methylnaphthalene (MNAP)	0.000 090 3	2.1	0.989	0.7-74

[a] Range of concentration used for calibration.

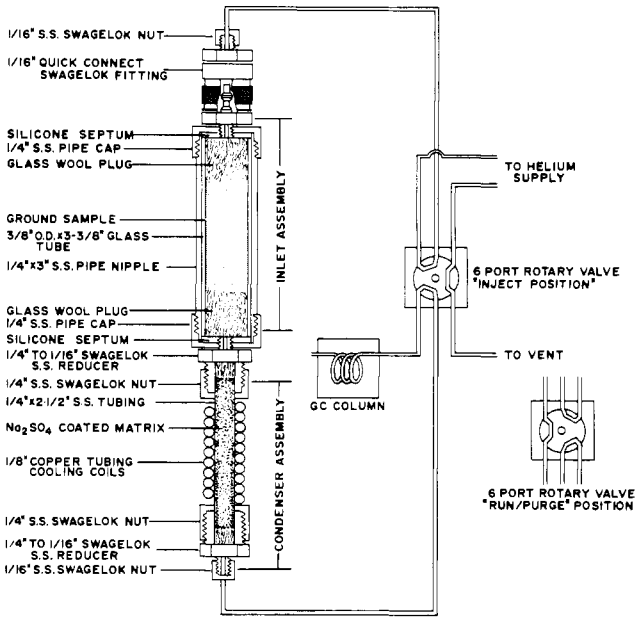

Figure 1. External inlet system for gas chromatograph–mass spectrometer.

positioning the tube between the two perforated silicone septums, forming a seal on both sides. With the rotary valve in the "inject" position, carrier gas was forced to flow down through the sample with the inlet at 120 °C. Volatile components were swept from the sample through the condenser assembly onto the head of the ambient, cooled GC column. After the 20-min elution period, the rotary valve was put into the "purge/run" position, the GC–MS interface valve was opened, and the GC oven was heated rapidly to 110 °C. Then the ion source and data system were turned on and the oven was temperature programmed to 220 °C at 10 °C/min. During the GC–MS run, a total of 500 scan (2 s each) of MID data were recorded on the DS disk for processing. While the run was in progress, the inlet was cooled and the condenser was heated to 130 °C to regenerate the condenser packing.

During analysis by MID, 11 different masses (40, 62, 76, 78, 83, 91, 117, 128, 142, 146, 180) were monitored. These masses (ions) are characteristic of acetonitrile, dimethyl sulfide, carbon disulfide, benzene, chloroform, toluene, carbon tetrachloride, naphthalene, methylnaphthalene, dichlorobenzene, and trichlorobenzene, respectively. A calibration mixture containing approximately 10 ppm of each of the 11 compounds was made up in a high-quality vegetable oil. Five different volumes of this calibration mixture, representing concentrations ranging from 10 to 100 ppb, were injected individually onto a 1-g spent sample (i.e., one which had been used for analysis) and analyzed. Two different volumes of a second calibration mixture

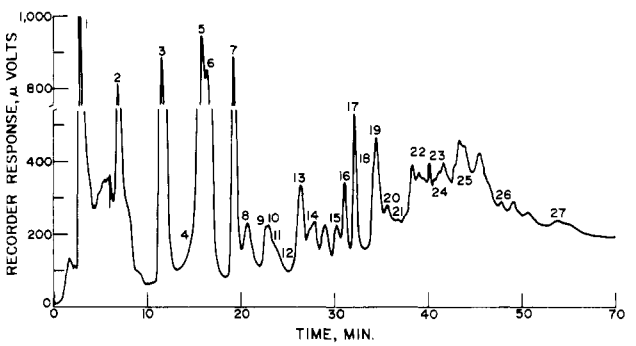

Figure 2. Profile of volatiles from snapea (Table I).

containing ca. 200 ppm of some compounds and 3 ppm of others were also used. Each compound was quantitatively characterized by its retention time and its ion peak area, which was computed by the data system. Table III shows the results of a linear regression analysis of the calibration data for each compound and the range of concentration. The concentrations of the 11 compounds were calculated for each sample by the formula concentration (ppb) = slope × area + Y intercept. These results are shown in Table IV. For methylnaphthalene, the combined area of the two isomers was used. Both isomers were present in the standard and in the samples.

RESULTS AND DISCUSSION

Semiquantitative Analysis. The conditions used for the semiquantitative portion of this work were similar to those used in the laboratory for peanuts (Brown et al., 1972). Inlet temperature was selected on the basis of preliminary tests, which showed that inlet temperature settings above 140 °C scorched the samples and that relatively long transfer times were required below 110 °C. Most of the volatiles were eluted in 5 min at 130 °C. Methanol was lost if transfer time was longer than 15 min. Rerunning spent samples verified that all of the moisture and 80–90% of the organic volatiles were removed in 10 min at 130 °C, and that there was little selective retention of the higher-boiling compounds. Attempts to use added water to improve recovery of volatiles (Fore and Dupuy, 1972) gave erratic results. Added water apparently promoted enzymatic reactions in the ground seed or resulted in hydrolysis during heating in the injection port. All of the southernpea samples contained about the same amount of water (10%), so any effects of water should be reasonably uniform throughout the series. Blank runs did not yield volatiles.

The thirty-two lots of southernpeas analyzed are described in Table I. A typical chromatogram is shown in Figure 2. Compounds identified by qualitative gas chromatography–mass spectrometry and measured semiquantitatively by gas chromatography are listed in Table

Table IV. Concentrations of Potential Toxicants in Southernpeas (ppb)

sample no.[a]	ACNL	DMSD	CDSD	CHLR	BNZN	TOLN	DCBZ	TCBZ	NAPH	MNAP
1	144.4	42.6	2.2	37.8	3.0	22.2	23.3	5.5	5.5	6.1
2	106.2	90.7	2.2	50.4	3.9	21.9	5.7	4.5	3.9	3.8
3	45.9	284.9	2.3	26.9	2.2	6.1	4.4	5.4	3.5	3.5
4	103.2	127.5	2.1	62.2	0.7	4.7	1.5	3.0	2.1	2.8
5	76.3	150.5	2.3	39.8	1.0	17.6	1.5	3.0	2.0	2.9
6	83.3	64.5	1.5	57.3	4.4	11.4	33.2	8.7	7.7	8.6
7	106.8	36.6	2.0	42.2	3.7	10.6	7.1	6.4	5.2	5.1
8	82.3	253.0	3.2	46.4	1.0	4.1	1.6	3.0	2.7	3.2
9	188.5	69.8	2.8	37.5	4.5	17.8	7.5	5.8	5.4	5.0
10	193.3	36.9	2.0	39.9	4.6	18.2	11.4	10.8	8.3	8.5
11	198.6	47.3	2.3	54.7	4.3	10.4	38.3	6.5	6.2	5.6
12	74.5	49.4	1.8	37.3	4.3	10.2	33.3	8.8	9.9	11.4
13	96.3	69.8	1.4	52.1	4.3	8.4	8.9	5.8	4.9	4.3
14	161.8	57.5	2.1	42.4	4.1	20.7	9.1	7.6	5.9	5.7
15	185.2	147.1	1.9	40.1	1.0	7.4	1.9	3.4	2.4	2.9
16	100.2	192.2	1.6	56.6	2.1	5.2	2.4	3.3	2.3	2.8
17	183.0	35.6	1.9	53.6	4.1	15.1	41.6	9.9	8.5	8.3
18	78.4	43.3	1.7	19.8	1.6	7.4	9.2	3.5	5.7	8.8
19	123.4	202.4	2.3	7.7	0.9	4.4	6.6	3.2	5.3	4.7
20[b]	124.3	30.3	1.8	34.9	3.1	7.7	22.1	4.1	5.6	5.2
21	309.6	23.0	2.6	30.4	2.8	22.9	16.5	3.8	3.5	3.4
22	96.2	71.0	2.5	14.6	1.1	17.1	1.6	3.2	2.0	2.8
23	86.7	50.3	2.7	27.8	2.3	7.5	9.7	4.5	3.6	3.5
24	50.5	93.9	3.4	21.3	1.1	3.7	1.8	3.6	2.3	3.0
25	103.5	302.0	1.9	53.7	2.1	12.3	122.2	4.7	11.3	37.7
26	132.3	262.9	2.3	8.6	1.4	8.3	87.2	3.6	11.9	10.6
27	205.3	113.3	3.1	68.1	3.9	10.3	62.7	8.9	13.4	20.1
28	120.5	28.2	2.4	35.1	5.8	10.3	7.6	5.8	4.9	4.9
29	146.5	33.8	2.2	45.9	4.4	9.3	9.9	10.9	5.9	4.7
30	135.6	35.6	1.9	39.6	5.5	14.0	141.3	5.0	10.2	12.1
31	82.2	535.0	2.7	31.7	3.2	12.1	9.5	9.1	11.0	24.8
32	119.9	1530.9	3.0	6.9	1.3	10.9	14.6	3.3	9.8	8.9
mean	126	168	2.3	38.2	2.9	11.6	23.6	5.6	6.0	7.7
SD	55	281	0.5	15.8	1.5	5.7	34.3	2.5	3.3	7.3
Cv	0.44	1.70	0.21	0.41	0.52	0.49	1.45	0.44	0.54	0.96
median	120	70	2.3	38	3.0	10.9	9.5	5.0	5.5	5.1

[a] See Table I for description. [b] This sample contained 35.3 ppb of carbon tetrachloride.

II, along with some statistical measures of the variation in amounts of each compound. Reproducibility of the method was demonstrated by Lovegren et al. (1978). The mean of the coefficients of variation (Cv) for the various volatiles, based on five portions of a single grinding of beans, was 0.13 with a standard deviation (SD) of 0.07. For seven replicate grindings from one lot of seed, Cv increased to 0.29 and SD to 0.11, indicating significant (3% level) within-lot variation. Lot-to-lot variations were much greater (Cv = 0.86, SD = 0.58. The semiquantitative nature of these data did not warrant a detailed statistical search for significant differences among groups of related samples, but some general conclusions can be drawn.

For 15 of the compounds, the ratio of the mean to the median is 1 to 1.25, indicating a fairly normal distribution with some skewing toward the high side; but for seven compounds it is greater than 1.9, indicating severe skewing. In general, compounds with such high ratios also have very high Cv's.

In some cases, there seems to be segregation into a major low-level group and minor high-level group, i.e., biomodal distribution. For example, 32 of the ethanol contents were between 550 and 1900 ppb and the other eight were between 4400 and 7300 ppb. Methanol, 2-methylpropanol, 1-butanol, toluene, 1-hexanol, acetophenone, and methylnaphthalene may also have bimodal distributions. For 2-pentanone, 1-pentanol, ethylbenzene, acetophenone, and methylnaphthalene, the highest content was over three times that of the next highest. In no case were all of the high values associated with any known grouping of the samples, such as the year grown or insect resistance.

Although most volatiles varied independently, some seemed to be interrelated. For example, the correlation coefficients (r) for 2-propanol vs. acetone, 2-butanol vs. 2-butanone, and methylpropanal vs. methylbutanal were 0.84, 0.73, and 0.83, suggesting common origins for each pair.

Qualitative Analysis. In addition to the compounds listed in Table II, *tert*-butyl alcohol was found by mass spectrometry as a broad peak in the acetone-to-methylpropanal region in some samples. Other compounds identified in some samples by mass spectrometry and their locations were: 3-methylbutanol, between 2-pentanone and 1-pentanol; dimethyl disulfide, ahead of toluene; and 2-pentylfuran ahead of benzaldehyde.

Some of the seeds had been stored in the presence of 2,2-dichloroethenyl dimethyl phosphate. Peaks that appeared ahead of hexanal and ahead of benzaldehyde in a few such samples were traced to this insecticide and were tentatively identified as dichloroacetaldehyde and dichloroethanol. Propylene glycol in one commercial sample and a series of unidentified GC peaks in another were traced to contamination from contact with the bag. Use of seed from the center of the bag eliminated these peaks.

Although we know of no other data on volatiles in southernpeas, methanol, acetaldehyde, ethanol, acetone, dimethyl sulfide, 2-methylbutanal, benzene, pentanal, 2- and 3-methylbutanol, 1-pentanol, toluene, hexanal, 1-hexanol, xylene, benzaldehyde, 2-pentylfuran, naphthalene, and methylnaphthalene have been reported in beans (Buttery et al., 1975; Johnson et al., 1971).

Quantitative Analysis. The new technique used for quantitative GC–MS–DS analysis for potential toxicants was developed to overcome deficiencies in the semiquantitative and qualitative techniques. Unfortunately, even semiquantitative estimates of important toxicants or

carcinogens such as chloroform, benzene, and dichlorobenzene could not be made by GC alone because they were not resolved. Since these compounds and several of the other constituents reported to be toxic (Christensen et al., 1974) or carcinogenic (Christensen et al., 1976) give uncommon ions as base peaks in their mass spectra, we attempted to determine their concentration by GC–MS–DS analysis. However, the procedure used for qualitative analysis was not satisfactory for quantitative analysis. Transfer of the volatiles from the sample to Porapak and then to the column resulted in poor recovery of some volatiles. Poorly heated areas in the injection port were a major cause of loss in both steps. In addition, the volume of carrier gas required to sweep all the water through the Porapak was large enough to elute some of the low-boiling volatiles. Further loss may have occurred when the injection port was opened to insert and remove the Porapak. With the auxillary inlet system, over 90% of the volatiles of interest was transferred to the column and 95% of the water was retained in the condenser. The sodium sulfate could be regenerated at least a hundred times.

The MS data system was used in the MID mode because this mode increases sensitivity. Since most potential interference were eliminated by proper selection of the ions being monitored, resolution of peaks could be sacrificed in favor of the shorter analysis time obtained with a more rapid temperature program. The base peaks, which give maximum sensitivity, were used for all compounds except acetonitrile. For acetonitrile, the second largest peak (m/e 40, rel intensity 50) was used because it is much more selective than the base peak (m/e 41), which is present in most spectra.

Similar responses were obtained for the standards when they were applied to glass wool instead of to spent samples. Reruns of the spent samples after transfer of the standards yielded no detectable amounts of most of the compounds and only traces of any of them. Nearly quantitative elution of the volatiles from the sample, therefore, was obtained.

The intercepts for the regression equations (Table III) are the minimum amounts that could be detected. These minimums might be increased by adjusting the MS–DS for higher sensitivity, but this could saturate the A/D converter at high concentrations, thereby flattening the tops of the peaks and rendering the data useless. As shown in Table IV, all toxicants except carbon tetrachloride were found in all southernpeas. Statistical analyses are given at the bottom of Table IV. As in the case of the GC results (Table II), some of the components show relatively little variation and fairly normal distribution at the low end of the range with much higher contents for a few samples. An exception is chloroform for which three samples are clustered at the low end of the range. For some of the components, the concentrations can be divided into two or more significantly different groups. For example, 30 of the benzene concentrations can be divided (99.9% confidence) into a group of 10 with a mean of 1.1, a group of 8 with a mean of 2.6, and a group of 21 with a mean of 4.2. The other two lie outside the range of the highest group.

A few duplicate runs indicated that the within-lot variation observed in the GC analysis applies to these volatiles. Further research will be required to determine whether any of the high or the low toxicant levels are genetic or are due to other causes. The source of the carbon tetrachloride observed in one sample could not be established.

Simple inspection of the data shows that most of the toxicant concentrations vary independently. However, there appeared to be some correlations between naphthalene and methylnaphthalene, between benzene and toluene, and between chloroform and trichlorobenzene. These correlations were confirmed by calculation of the appropriate regression equations and correlation coefficients (r = 0.77 for the first pair, 0.38 for the second pair, and 0.34 for the third pair). The naphthalene–methylnaphthalene correlation increased to 0.93 when samples 25 and 31 were omitted. Similarly, the benzene–toluene correlation increased to 0.52 when samples 5 and 22 were omitted. On the other hand, r was less than 0.1 for dichlorbenzene vs. trichlorobenzene.

CONCLUSIONS

No significant relation between the variations in concentration of the various toxic and nontoxic volatiles and type of southernpea, year of growth, insect resistance, or place of growth was found. Damaged, moldy, and insect-damaged seeds removed before samples were taken for analysis did show some significant differences, e.g., one such sample did not contain naphthalene or methylnaphthalene.

The GC–MS–DS technique with multiple ion detection should be easily adaptable for analysis of other foods and feeds for volatile potential toxicants.

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Received for review May 26, 1978. Accepted August 28, 1978. Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.