Bull. Environm. Contam. Toxicol. 21-563-568 (1979)

# Residues of Tetrachloronitrobenzene and Related Compounds in Potatoes

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Tetrachloronitrobenzene (TCNB, Fusarex$^R$, Tecnazene$^R$) is used as a sprout suppressant on potatoes. The recommended application rate for Fusarex$^R$ (6% TCNB) is 1.0 lb. for each 600 lbs. of potatoes. Residues of TCNB have been found during the examination (by gas chromatography) of several potato composites from the Total Diet Program conducted by the Food and Drug Administration (MANSKE and JOHNSON 1977). These chromatograms often contain several other peaks thought to be related to TCNB. The identity of these compounds has been determined by mass spectrometry (GC/MS).

## EXPERIMENTAL

Routinely, the boiled, fried and baked potatoes from each market basket were examined as a composite. However, these three categories of cooked potatoes from one market basket were analyzed individually. In all cases, the boiled and fried potatoes were peeled prior to cooking. The baked potatoes, however, were cooked and composited unpeeled.

The official methods currently used by the Food and Drug Administration for multiresidue analysis were applied:

(a) The homogenized composite was blended with acetonitrile and filtered. The filtrate was diluted with water and extracted with petroleum ether (AOAC, par 29.011 (a), 1975).

(b) Cleanup of the petroleum ether extract was accomplished with a Florisil column (MILLS et al. 1972). Both eluant A (20% $CH_2Cl_2$-hexane) and eluant B (50% $CH_2Cl_2$-0.35% acetonitrile-49.65% hexane) were analyzed by gas chromatography with electron capture detection (EC/GC).

EC/GC: A Tracor 222 gas chromatograph with a $^{63}Ni$ detector and linearizer was used for quantitative analysis. Column parameters were as follows:

0007-4861/79/0021-0563 $01.20

Pyrex, 1.8 m x 4 mm (ID) packed with 3% OV-1 on Chromosorb WHP 80/100 mesh at 130°, with a carrier gas of 5%/95% methane in argon at 50ml/min flow.

GC/MS: A DuPont 491B mass spectrometer was interfaced through a glass jet separator to a Packard 838 gas chromatograph. Samples were injected on a 1.8 m x 2 mm pyrex column packed with 3% OV-1 on Chromosorb WHP 60/80 mesh at 130° and 30 ml/min He flow. The injector temperature was 220°.

The data system was comprised of a Hewlett-Packard 2100A computer (16K), and 7900A disc drive, with Tektronix 4010 teletype port interface and 4610 hard copy unit.

Electron impact spectra (75 eV) were obtained at a scan rate of 2 sec/dec, scanning from 517 to 41 amu. The source was held at 240° with an accelerating voltage of 1.4 KV.

## RESULTS AND DISCUSSION

The compounds found in potatoes are listed in Table 1. Their retention data, relative to pentachlorobenzene (QCB) is included.

TABLE 1
Compounds found in potatoes

| Identity | relative retention (QCB = 1.00; 6.5 min) 3% OV-1, 130° |
|---|---|
| Tetrachlorobenzene[1] | 0.40 |
| Trichloronitrobenzene[2] | 0.86 |
| 2,3,5,6-Tetrachloroanisole | 1.02 |
| Tetrachloronitrobenzene (TCNB)[3] | 1.37 |
| Tetrachloroaniline (TCA)[4] | 1.50 |
| Tetrachlorothioanisole (TCTA)[5] | 2.72 |
| Pentachloronitrobenzene (PCNB) | 2.98 |
| Tetrachloro-p-nitroanisole | 3.45 |
| Tetrachloro-p-anisidine | 3.63 |

[1] 1,2,4,5- and/or 1,2,3,5-tetrachlorobenzene, relative retentions of these two isomers are identical.

[2] Relative retention identical to 1,2,4-trichloro-5-nitrobenzene

[3] Relative retention identical to 2,3,5,6-tetrachloronitrobenzene

[4] Relative retention identical to 2,3,5,6-tetrachloroaniline

[5] Relative retention identical to 2,3,5,6-tetrachlorothioanisole

Since all the positional isomers of trichloronitrobenzene, TCNB, TCA, and TCTA were not available an unambiguous identification of these four compounds could not be made.

Of the compounds in Table 1, tetrachloro-p-anisidine was found in eluate B and tetrachloro-p-nitroanisole was found in both eluate A and eluate B. The remaining compounds all appeared in eluate A.

An assay of Fusarex$^{R}$ (6% TCNB) was performed. The commercial product was simply diluted with ethyl acetate to a concentration compatible with electron capture sensitivity. The results of this assay are given in Table 2.

TABLE 2
Assay of Fusarex$^{R}$

| Identity | ppm |
|---|---|
| Tetrachloronitrobenzene (TCNB)[1] | 58,300 (5.83%) |
| Trichloronitrobenzene[2] | 570 |
| Tetrachlorobenzene[3] | 383 |
| Pentachloronitrobenzene (PCNB) | 280 |
| Pentachlorobenzene (QCB) | 14 |

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[1] Calculated as 2,3,5,6-tetrachloronitrobenzene
[2] Calculated as 1,2,4-trichloro-5-nitrobenzene
[3] Calculated as 1,2,4,5-tetrachlorobenzene

Quantitative analysis of two potato composites are listed in Table 3. Identification or confirmation was performed utilizing GC/MS.

The compounds in Table 3 have relative retentions (EC/GC) identical to that of the isomer listed in their respective footnotes.

The boiled, fried, and baked potatoes from one market basket were examined individually. Table 4 contains the results of these analyses.

The compounds in Table 4 have relative retentions (EC/GC) identical to that of the isomer listed in their respective footnotes.

It is suspected that the baked potatoes showed a higher level of these compounds because they were not peeled before being analyzed as were the boiled and fried potatoes.

Unambiguous identification and quantitation of these compounds could only be made when all positional isomers were available as standards. Therefore, all the isomers of tetrachloroanisole, tetrachloronitroanisole, and tetrachloroanisidine were synthesized. The individual isomers of tetrachlorophenol were methylated with diazomethane to form their respective tetrachloroanisoles. Using a procedure described by PETERS et al.

## TABLE 3

Results of analysis of two potato composites by EC/GC
Values are expressed in ppm

| Identity | Composite 1 | Composite 2 |
|---|---|---|
| Tetrachloronitrobenzene (TCNB)[1] | 0.059 | 0.281 |
| Tetrachlorobenzene[2] | 0.003 | 0.055 |
| Trichloronitrobenzene[3] | - | T |
| 2,3,5,6-Tetrachloroanisole | - | T |
| Tetrachloroaniline (TCA)[4] | 0.008 | 0.036 |
| Tetrachlorothioanisole (TCTA)[5] | 0.002 | 0.002 |
| Pentachloronitrobenzene (PCNB) | - | T |
| Tetrachloro-p-nitroanisole | - | T |
| Tetrachloro-p-anisidine | 0.012 | 0.030 |

1 Calculated as 2,3,5,6-tetrachloronitrobenzene
2 Calculated as 1,2,4,5-tetrachlorobenzene
3 Calculated as 1,2,4-trichloro-5-nitrobenzene
4 Calculated as 2,3,5,6-tetrachloroaniline
5 Calculated as 2,3,5,6-tetrachlorothioanisole
T= Trace (less than could be calculated accurately)

## TABLE 4

Results of analysis of boiled, fried, and baked potatoes from one market basket analyzed individually. Values are expressed in ppm.

| Identity | boiled | fried | baked |
|---|---|---|---|
| Tetrachloronitrobenzene (TCNB)[1] | 0.278 | 0.214 | 1.84 |
| Tetrachlorobenzene[2] | 0.095 | 0.051 | 0.110 |
| Trichloronitrobenzene[3] | - | - | T |
| 2,3,5,6 Tetrachloroanisole | 0.002 | 0.001 | 0.003 |
| Tetrachloroaniline (TCA)[4] | 0.049 | 0.062 | 0.141 |
| Tetrachlorothioanisole (TCTA)[5] | 0.009 | 0.009 | 0.036 |
| Pentachloronitrobenzene (PCNB) | - | - | 0.003 |
| Tetrachloro-p-nitroanisole | - | - | T |
| Tetrachloro-p-anisidine | 0.050 | 0.060 | 0.088 |

1 Calculated as 2,3,5,6-tetrachloronitrobenzene
2 Calculated as 1,2,4,5-tetrachlorobenzene
3 Calculated as 1,2,4-trichloro-5-nitrobenzene
4 Calculated as 2,3,5,6-tetrachloroaniline
5 Calculated as 2,3,5,6-tetrachlorothioanisole
T= Trace (less than could be calculated accurately)

(1943) these compounds were then treated with nitric acid to form all three isomers of tetrachloronitroanisole which, in turn, were reduced to the corresponding tetrachloroanisidines with sodium hydrosulfite. Retention data for these compounds is contained in Table 5.

TABLE 5
Relative retentions of synthesized standards

| Identity | relative retentions (QCB = 1.00; 6.5 min) 3% OV-1, 130° |
|---|---|
| 2,3,4,5-Tetrachloroanisole | 1.87 |
| 2,3,4,6-Tetrachloroanisole | 1.03 |
| 2,3,5,6-Tetrachloroanisole | 1.02 |
| Tetrachloro-o-nitroanisole | 3.15 |
| Tetrachloro-m-nitroanisole | 3.33 |
| Tetrachloro-p-nitroanisole | 3.45 |
| Tetrachloro-o-anisidine | 4.29 |
| Tetrachloro-m-anisidine | 3.81 |
| Tetrachloro-p-anisidine | 3.63 |

TCA, TCTA, 2,3,5,6-tetrachloroanisole, tetrachloro-p-nitro-anisole and tetrachloro-p-anisidine were found in potatoes only when accompanied by TCNB residues. Since these five compounds are not present as impurities in Fusarex$^{R}$ (see Table 2) they are assumed to be metabolites of TCNB.

Evidence of an additional compound was found in the potatoes examined. GC/MS data showed an isotopic cluster characteristic of three chlorine atoms at m/e 271, 273, 275. This compound occurred in eluate B and had a relative retention of 3.6 (QCB = 1.00). Because of the small amount present and its proximity to tetrachloro-p-anisidine, positive identification was not achieved. However, it is speculated this compound may be trichloronitrothioanisole.

Specific recovery data of TCTA, 2,3,5,6-tetrachloroanisole, tetrachloro-p-nitroanisole, and tetrachloro-p-anisidine through the extraction and cleanup procedure has not been obtained. However, good recovery (80-100%) has been observed for similar compounds such as TCNB, PCNB, QCB and tetrachlorobenzene.

The mass spectrum of tetrachloro-p-nitroanisole (Figure 1) exhibits a strong molecular ion (67%) at m/e 289. The prominent M-30 ion is assumed to be the rearrangement peak characteristic of aromatic nitro compounds. The remaining fragmentation is consistent with the structure of tetrachloro-p-nitroanisole.

The prominent ions in the mass spectrum of tetrachloro-p-anisidine (Figure 2) are M-15 (80%) and M-43 (19%), as well as the molecular ion m/e 259 (28%). The

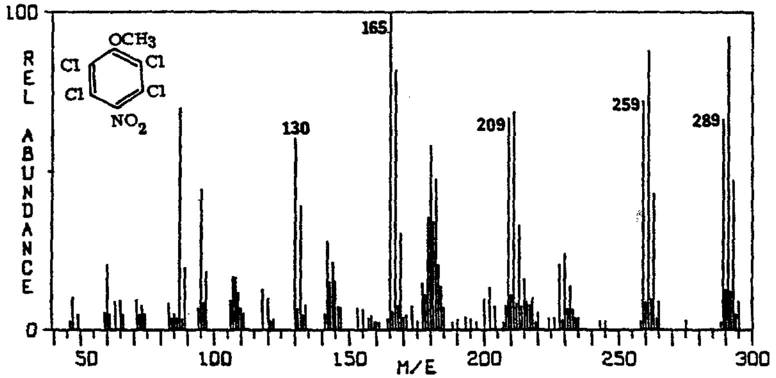

Figure 1 - Electron impact mass spectrum of tetrachloro-p-nitroanisole.

formation of these ions is probably due to the loss of the methyl group followed by the loss of carbon monoxide. The same fragmentation pattern is present in the spectra of the isomers of tetrachloroanisole.

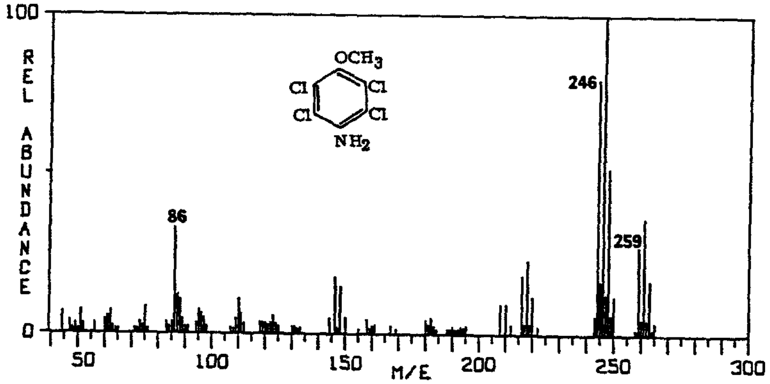

Figure 2 - Electron impact mass spectrum of tetrachloro-p-anisidine.

## ACKNOWLEDGEMENT

The authors thank Robert Jacobson for plotting the spectra, and the Hilton-Davis Company for the Fusarex$^{R}$.

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