

FOOD ANALYSIS IN THE DEPARTMENT OF ANALYTICAL CHEMISTRY AT THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION



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Pesticide Residues in Food – Keeping Current with New Products



The Answer to this is Simple Follow The.....

- The US EPA Defines a **Pesticide** as “...any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest.”
- A **Tolerance** is “...is a commodity-specific federally established upper limit to the amount of a chemical's residue allowed on a commodity. This can be on a raw agricultural commodity, and now applies uniformly to fresh and processed food or feed commodities...”
- **Adulterated Food** is defined, in part, “...as food that has a pesticide chemical residue that does not meet the safety standard of FFDCa sec.408.”

Pesticides Make Their Appearance In The US

- 1854 **Sulfur** Tobacco Dip Used – Sheep Scab
- 1861 **Hellebore** Used As Insecticide – Cabbage Worm
(Nightshade, Hemlock, Aconite)
- 1867 **Paris Green** – Arsenical Colorado Potato Beetle
- 1870's **Carbolic Acid** – Insecticide
 - Potash Solution** – Control Scale Insects
 - Petroleum** – Insect Bites & Stings
 - Kerosene** – Woolly Apple Aphid
 - Carbon Bisulfide** – Fumigant for Insect Control
 - London Purple** – Colorado Potato Beetle
- 1880's **Lime - Sulfur** – San Jose Scale
 - Coal Oil Emulsion** – 1st Contact Insecticide

Pesticides Make Their Appearance

- 1880's **White Arsenic** – Codling Moth
Naphthalene – 1st Used to Control Insects
Baits – Containing Poisons Introduced
Hydrocyanic Acid Gas – (HCN) – Fumigant
Lime-Sulphur-Salt – Used Against Scale
- 1885 **Pyrethrum** - Imports 622,114 pounds
- 1888 **California Pyrethrum** - Production 52 Tons
- 1891 **Lead Arsenate** – 1st Used as Insecticide
Creosote Oil – Ovicide for Gypsy Moth
- 1892 **Dinitrophenols** – Used in Germany as Insecticides

Regulating Adulterated Food Prior to the 20th Century

- **States had only the authority to control produce grown within their boundaries.**
- **The Federal Government was under public pressure to oversee the use of pesticide chemicals. By 1906 nearly 100 Bills had been passed in Congress to address interstate shipment of adulterated foods.**
- **1895 With Public Pressure Mounting, Connecticut Becomes Pro-Active in Protecting its Public from Adulterated Food. The State Legislature Passes a Public Act:**

Public Acts, January 1895

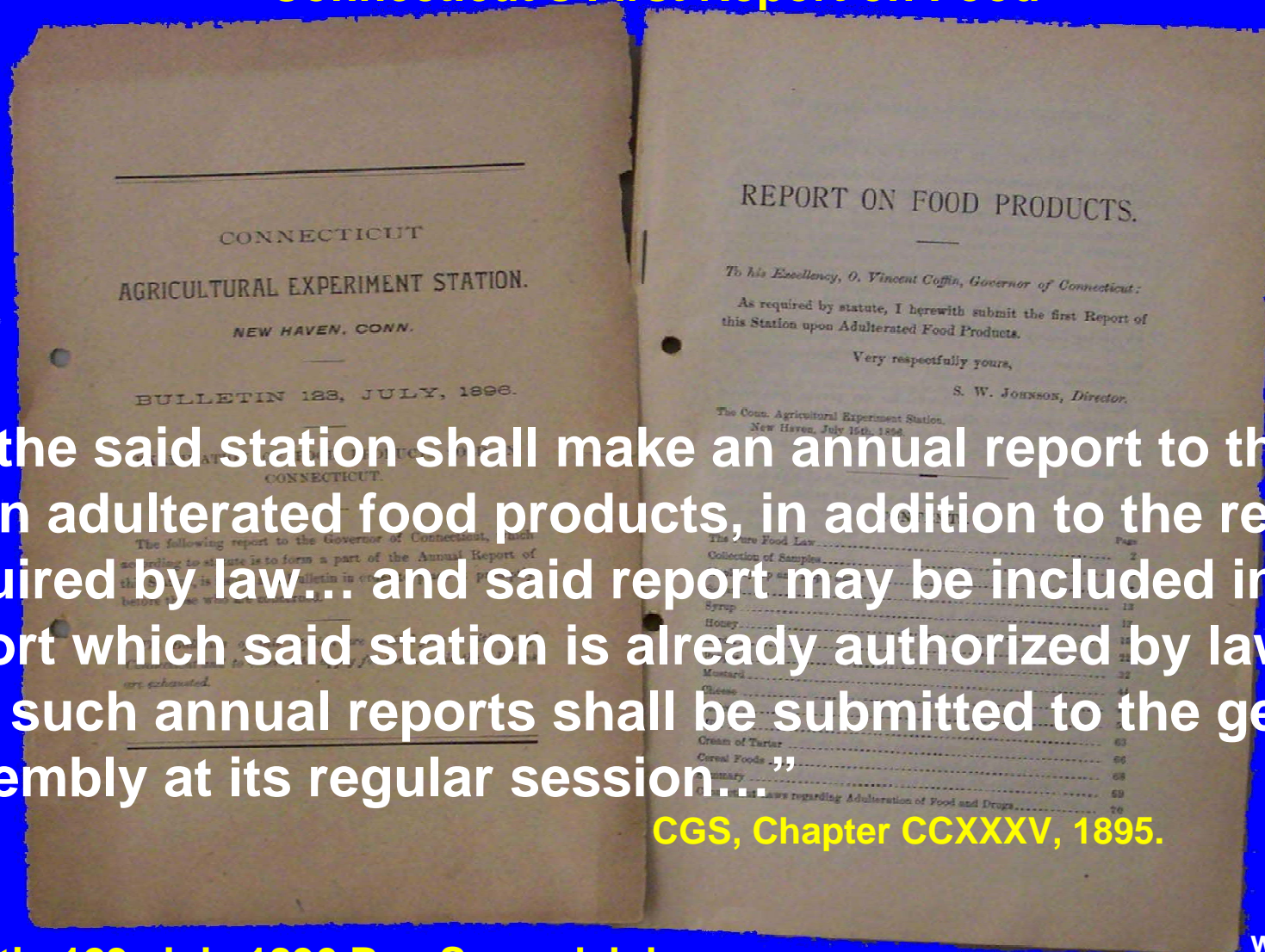
An Act regulating the Manufacture and Sale of Food Products

“Sec. 4. *The Connecticut Agricultural Experiment Station shall make analysis of food products on sale in Connecticut suspected of being adulterated, at such times and places and to such extent...may take from any person...any article suspected of being adulterated... and the said station may adopt or fix standards of purity, quality, or strength when such standards are not specified or fixed by Statutes.*”

CGS, Chapter CCXXXV, 1895

“Public Acts, January 1895

An Act regulating the Manufacture and Sale of Food Products” Connecticut’s First Report on Food

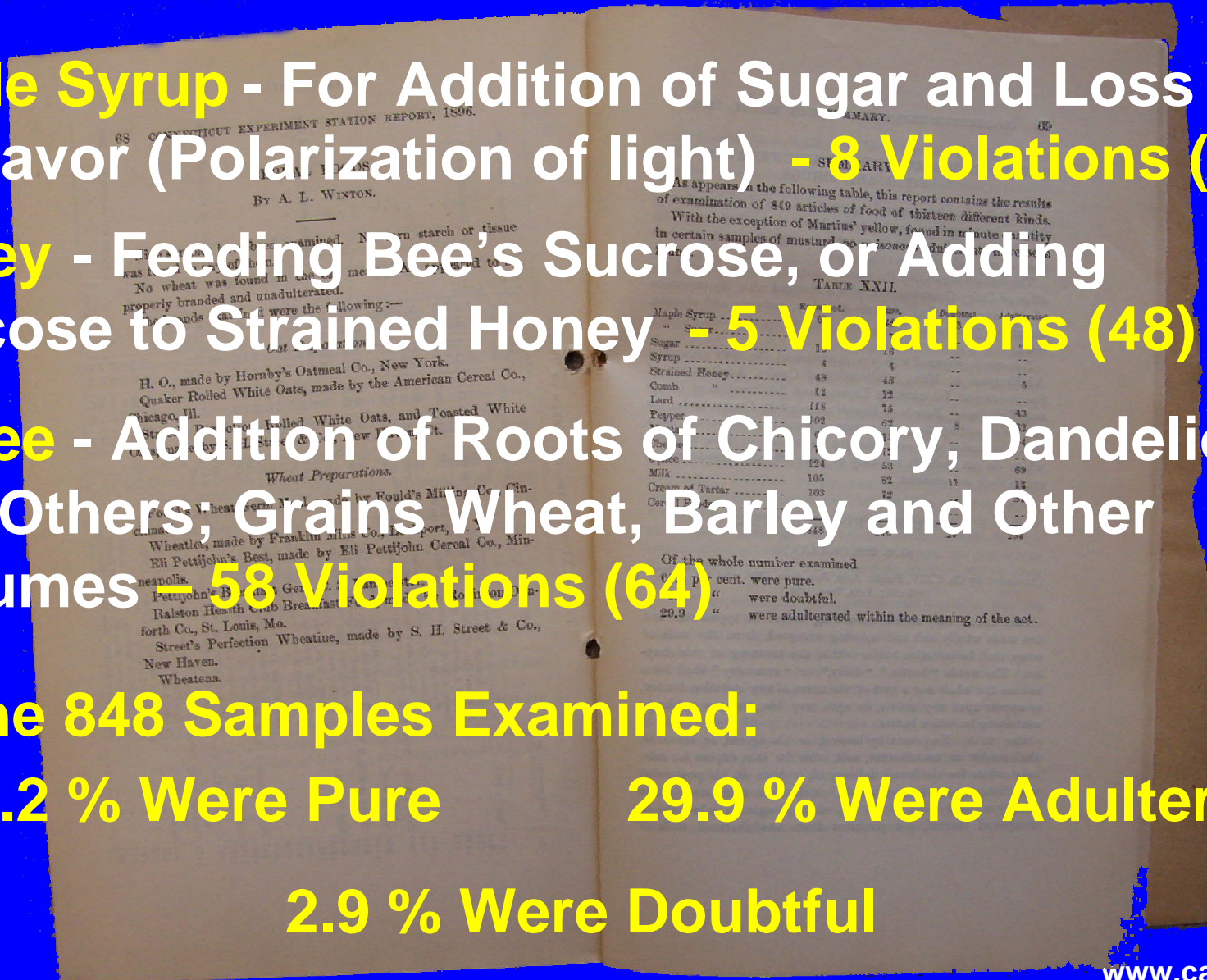


“... the said station shall make an annual report to the governor upon adulterated food products, in addition to the reports required by law... and said report may be included in the report which said station is already authorized by law to make, and such annual reports shall be submitted to the general assembly at its regular session...”

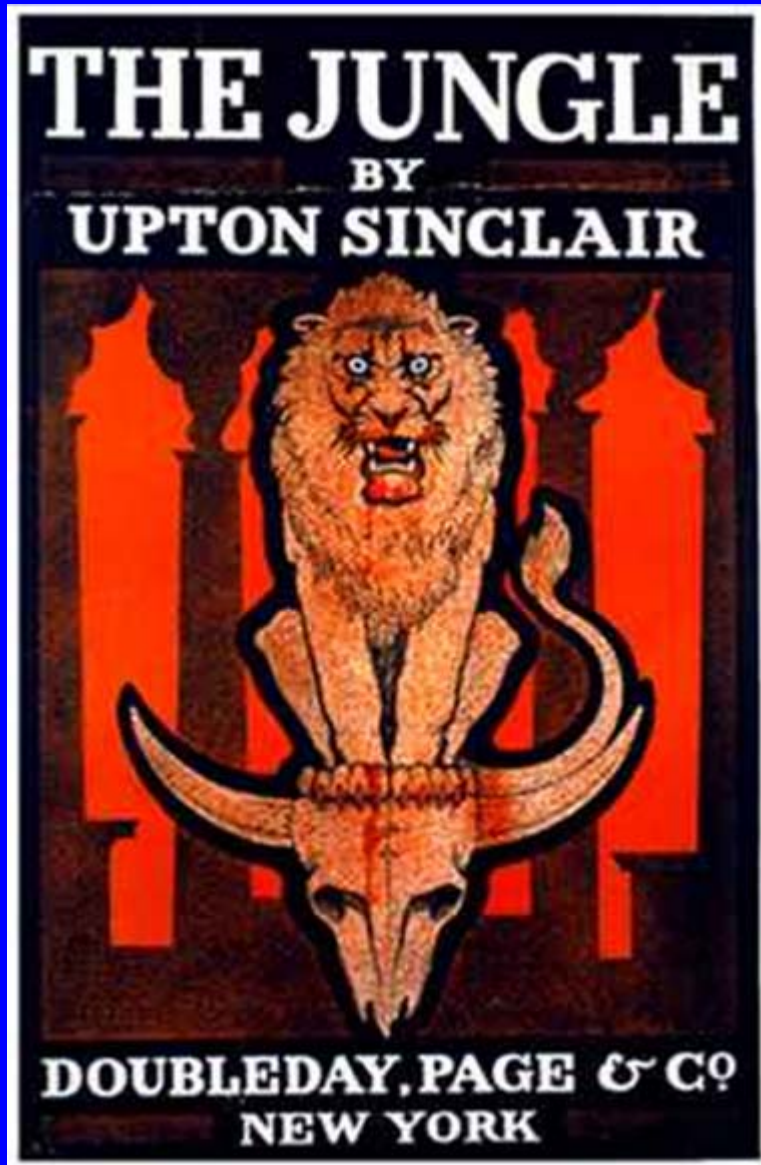
CGS, Chapter CCXXXV, 1895.

Results of the First Connecticut Study

- **Maple Syrup** - For Addition of Sugar and Loss of Flavor (Polarization of light) - **8 Violations (61)**
- **Honey** - Feeding Bee's Sucrose, or Adding Glucose to Strained Honey - **5 Violations (48)**
- **Coffee** - Addition of Roots of Chicory, Dandelion, and Others, Grains, Wheat, Barley and Other Legumes - **58 Violations (64)**
- **Of the 848 Samples Examined:**
 - 67.2 % Were Pure**
 - 29.9 % Were Adulterated**
 - 2.9 % Were Doubtful**



Public Outcry for US Standards



- 1905 Upton Sinclair's *The Jungle* is Credited as THE Major Factor to the 1906 Legislation.
- 1879 – 1906 Over 100 Bills Introduced in Congress to Regulate Food and Drugs
- 1906 Food and Drug Act (Wiley Act)
Keep Contaminated Food Off The Table

The List of Pesticides Continues to Grow

- 1896 **Sodium Fluoride** – 1st Used as Insecticide
- 1897 **Oil of Citronella** – 1st Used as Insect Repellent
- 1898 **HCN** – 1st Used to Control Home Insects
- 1912 **Paradichlorobenzene** – 1st Used in US
- 1918 **Magnesium Arsenate** – 1st Used as insecticide
- 1922 **Rotenone** – 1st Used as Insecticide
- 1923 **Carbon Tetrachloride and Ethylene Oxide** 1st Used
- 1923 **Selenium** – 1st used as Insecticide
- 1938 **Methyl Bromide** – 1st Used as Fumigant
- 1938 **Xanthone** – 1st Used as Insecticide

1934 Pesticide Usage

| Chemical Type | Pounds (Millions) |
|--------------------------------------|-------------------|
| Arsenicals | 80 - 90 |
| Sulfur | 73 |
| Kerosene | 10 |
| Mineral Oil Emulsion | 40 |
| Creosote Oil (Wood) | 106 |
| Petroleum Oil (Wood) | 20 |
| Napthalene, p-Dichlorobenzene | 21 |
| Pyrethrum | 10 |
| Nicotine Sulphate | 2 |
| Rotenone | 1.5 |

False Claims Become a Problem

➤ With FDR's election, the FDA had a receptive ear for the legally mandated quality and identity standards for food products and prohibition of false claims.

FDA Exemplified the shortcomings of the 1906 Law

- Lash Lure – Eyelash Blinding Some Woman
- Radithor – Radium containing Poison Meaning Death to its users
- Thalidomide -- 1937 Incident. The Drug Elixir contained the solvent of glycol, untested in humans resulting in over 100 deaths



Development In The 1940's & 1950's

- **1944 Colorimetric Analytical Method for Rotenone**
- **1950 Gas Masks and Respirators Introduced for Worker Protection**
- **1952 Colorimetric Test For BHC Analysis**
- **1952 James and Martin (Nobel Laureate) work leads to commercial gas-liquid chromatography**
- **May 1955 Perkin-Elmer began to sell America's first commercial gas chromatograph, the Model 154**
- **1958 Delaney Clause (Paradox) to FFDCA**
- **1959 Aminotriazole Cranberry Scare**



The 1960's

➤ 1962 – Rachel Carson's *Silent Spring*

“Over increasingly large areas of the United States, spring now comes unheralded by the return of the birds, and the early mornings are strangely silent where once they were filled with the beauty of bird song.”

(Rachel Carson)

Why?

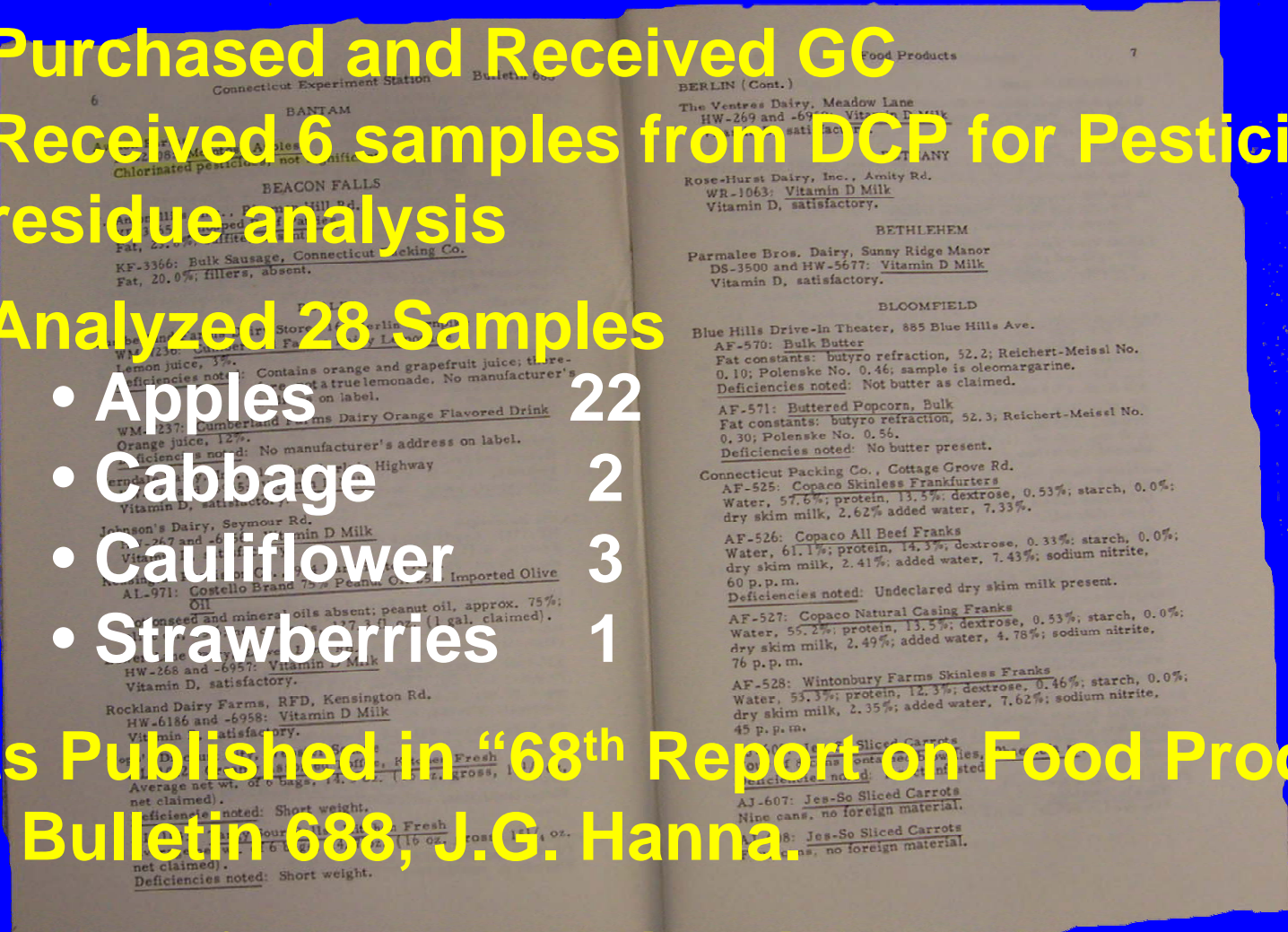
Because of US!



➤ 1960's Widespread commercialization of GC provides methods for the routine analysis of pesticide residues in food

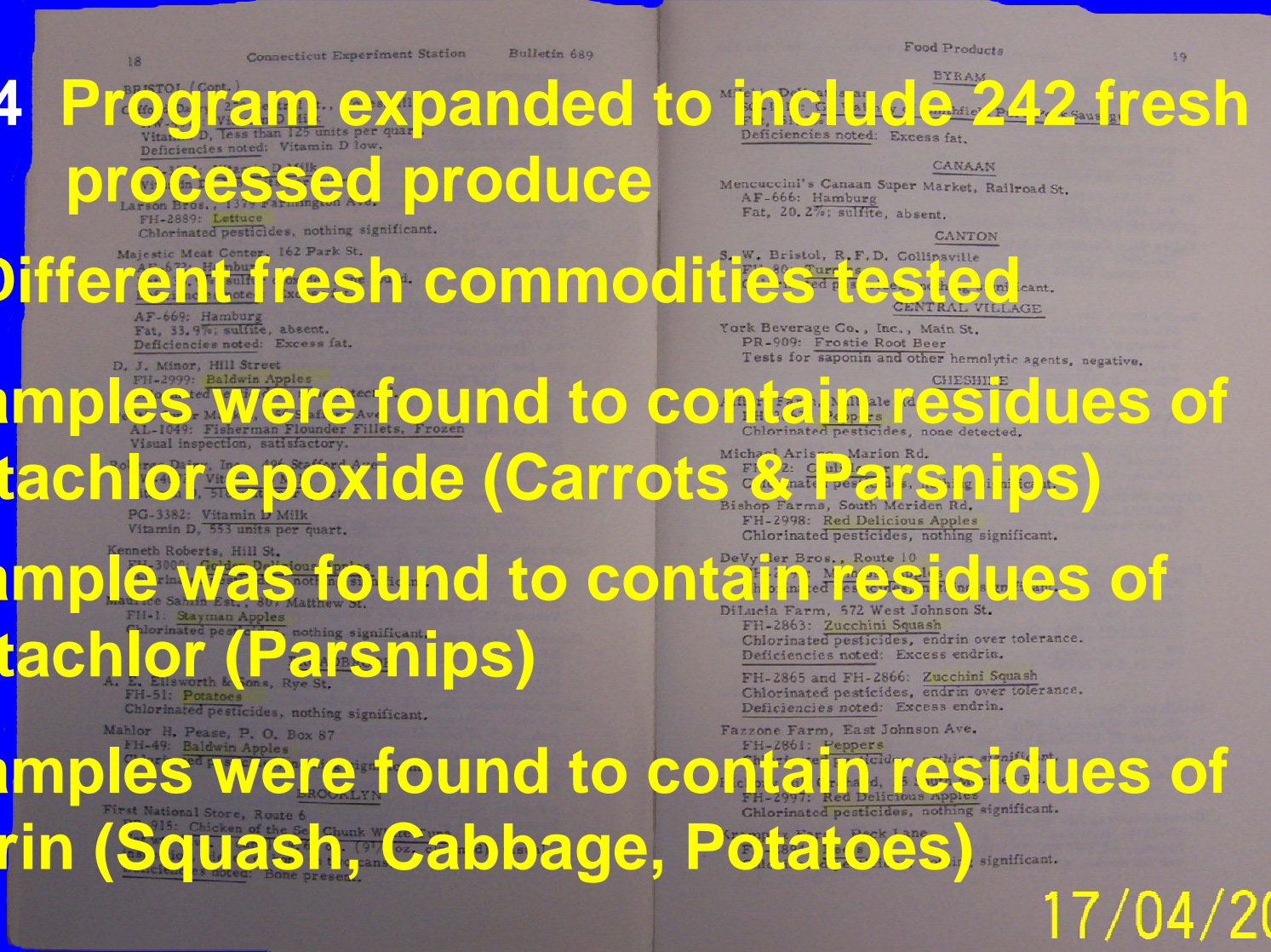
1960's at CAES

- 1962 Purchased and Received GC
- 1962 Received 6 samples from DCP for Pesticide residue analysis
- 1963 Analyzed 28 Samples
 - Apples 22
 - Cabbage 2
 - Cauliflower 3
 - Strawberries 1
- Results Published in "68th Report on Food Products 1963" Bulletin 688, J.G. Hanna
- NO Samples found to be Violative



Program Expanded in 1964

- **1964** Program expanded to include 242 fresh processed produce
- **19** Different fresh commodities tested
- **2** Samples were found to contain residues of heptachlor epoxide (Carrots & Parsnips)
- **1** Sample was found to contain residues of heptachlor (Parsnips)
- **8** Samples were found to contain residues of endrin (Squash Cabbage, Potatoes)



17/04/20

Structure of Food and Drug Regulation

EPA – Registers and sets Tolerances for pesticide chemicals

- Responsible for pesticides in ground water

FDA – Analyzes food and vegetables for pesticides and enforces food Tolerances.

- Responsible for the registration of drugs

USDA – Maintains statistics and records on pesticide use.

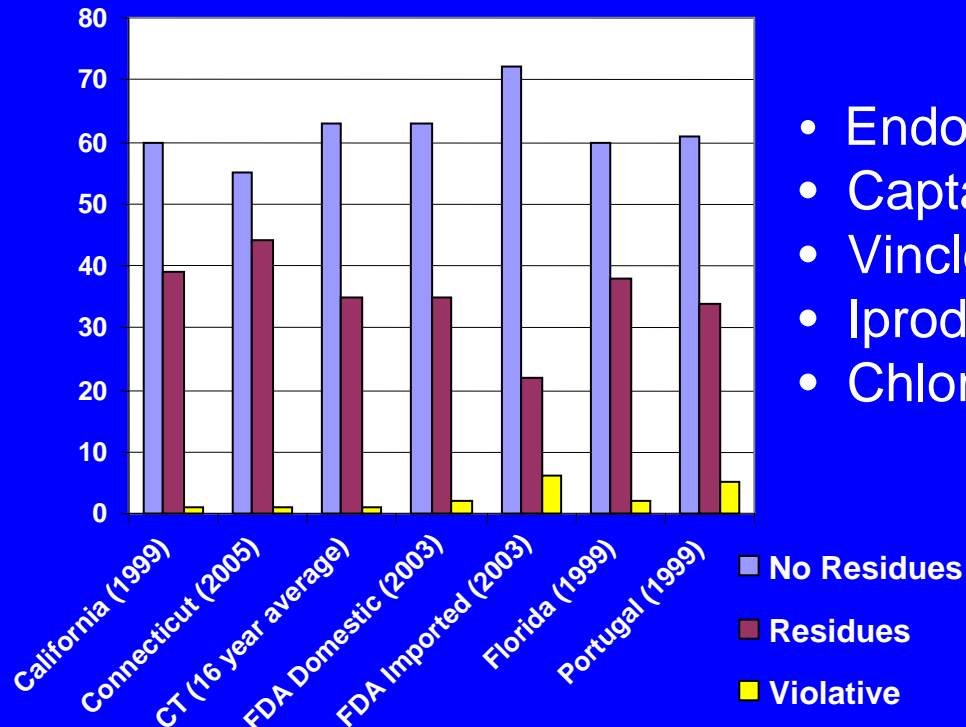
- Responsible for monitoring and enforcing Tolerances on poultry, and dairy products

Market Basket Survey



Annual Market basket Survey

- 16 year survey of produce sold in Connecticut for pesticide residues in food to supplement FDA monitoring program.
 - Analyzed 4844 samples since 1990. FDA analyzed 34 samples from Connecticut since 1993. (927 samples reported 1992 – 93).
 - CT averages 305 samples / yr.; 63% contain NO residues, 35% contain legal residues, 1.4% contain illegal residues.



CT

- Endosulfan (27%)
- Captan (16%)
- Vinclozolin (7.3%)
- Iprodione (6.2%)
- Chlorthalonil (6.0%)

2003 FDA*

- DDT (12%)
- Malathion (7%)
- Endosulfan (7%)
- Dieldrin (6%)
- Chlorpyrifos (6%)

* As Part of Total Diet Study

2005 Findings

- **163 Samples** of fresh and processed produce tested
- **93 (57%) Samples** contained **NO** residues
- **67 (41%) Samples** contained residues within Tolerance
- **3 (2%) Samples** were No Tolerance Violations
 - **All produced in Connecticut**
 - **Ronilin®** found on Strawberries (0.08 ppm)
 - **Chlorothalonil** found on Apples (0.056 ppm)
 - **Chlorothalonil** on Bell Peppers (0.06 ppm)

2002-2004 Bulletin

*The
Connecticut
Agricultural
Experiment
Station,
New Haven*

Pesticide Residues
in Produce Sold in
Connecticut
2002-2004

BY WALTER J. KROL,
TERRI ARSENAULT, AND
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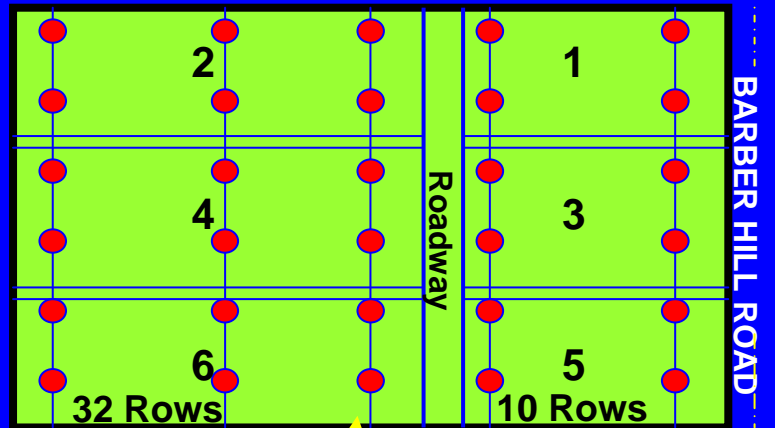
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- **Please feel free to contact me: **Walter J. Krol, Ph.D.** (203) 974 - 8456**
- **Thanks to: Terri Arsenault
Dr. Mary Jane Mattina &
Analytical Chemistry Staff**

State Agencies Working Together

- In late July, DCP inspector delivered 4 samples of fresh produce for analysis
- Two samples contained no residues, 2 contained residues of chlorothalonil
- Tolerance for one, but not the Bell Peppers
- Inspectors from DCP and DEP interviewed the grower
- Application was made by contract with a third party also made to eggplant
- Would result in Violation if crop harvested for sale
Grower voluntarily plowed the crop under

PESTICIDE BARN *FIRE* NEAR STRAWBERRY FIELD June, 2005



Southerly Wind

- *FIRE* in barn adjacent to strawberry field.
- Barn contained pesticides.
- Harvesting underway.
- State banned sale pending sampling and analysis.
- Samples released Monday June 13th, 2005.

- Individual samples received and analyzed from each of 6 different fields, June 10th.
- Samples contained: captan (0.3 – 0.36), T=25; endosulfan (0.1 – 0.13) T=2; cyprodinil (0.1 – 0.13), T=5; fludioxonil (0.1 – 0.2), T=2. (ppm).
- Samples did NOT contain: carbaryl, pyraclastroben, metaldehyde or glyphosate.
- Admitted to legal application of other pesticides, which were also in barn.

Active Ingredients with Food Tolerances

March 21, 2006 **360** Chemicals with Food Tolerance

186 Substances Exempt from food Tolerance

| YEAR | Number AI Registered for Food Use |
|------|-----------------------------------|
| 2005 | 355 |
| 2004 | 352 |
| 2003 | 340 |
| 2002 | 336 |
| 2001 | 337 |
| 2000 | 323 |
| 1999 | 320 |
| 1998 | 341 |