# Chromium and Nickel in Acidic Foods and By-Products Contacting Stainless Steel During Processing

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There has been much speculation but little published data concerning the possible extent of metal contamination of acidic foods and their by-products as a result of their contact with metal surfaces. For instance, elevated concentrations of Sn and Zn in honey have been attributed to its processing in an extractor having galvanized surfaces (TONG et al. 1975). Food processing equipment is most commonly constructed of stainless steel which contains Cr, Ni and other elements (LANGE 1949). Continued use of such equipment with acidic foods might result in the release of appreciable quantities of these elements. The present study consisted of a survey of a variety of acidic foods which had been in contact with stainless steel surfaces during harvesting, processing and/or preparation for market. Chromium and Ni were determined in these foods as a possible indication of the release of these elements from this exposure.

### EXPERIMENTAL

The food samples collected locally included acidified red cabbage, sauerkraut, honey, vinegar, cheese whey and wine. With the exception of the comb honey (see Table 2), all of the samples had contacted stainless steel surfaces. The cabbage sample consisted of 12, 1-lb glass containers of the product. These were mixed together, in a plastic container and subsampled for analysis of both solids and brine. Similarly, 24, 27-oz enameled cans of sauerkraut were mixed and subsampled prior to determination of Cr and Ni. The sauerkraut in flexible pouches consisted of 12, 2-lb packages which were mixed and subsampled prior to analysis. All of the other commodities were obtained as single samples.

The methods used for drying and ashing the samples are listed in Table 1. Chromium was determined by wet ashing the samples using sulfuric and nitric acids and hydrogen peroxide (ANALYTICAL METHODS COMM. 1960) followed by chelation (CARY and ALLAWAY 1971) and determination by furnace atomic absorption analysis (CARY and OLSON 1975). Nickel was determined by dry ashing and furnace atomic absorption analysis (ZACHARIASEN et al. 1975). The pH of the cheese whey was taken on a 7% aqueous suspension of the product.

## RESULTS AND DISCUSSION

The results of analysis of the samples for Cr and Ni are given in Table 2. With the exception of red cabbage brine the concentrations of these elements in the various liquid food products was

quite low. The concentration of Cr in the wine stored in redwood was somewhat elevated as compared to that in the other wines. Interestingly the honey analyzed directly from the comb was somewhat lower in Cr but as high or higher in Ni than the other honey samples. The hard cider sample was somewhat lower in both elements than the vinegar made from it.

TABLE 1
Methods used for drying and ashing samples

methods used	1 TOL GL	ying and asni	ng sampres	•	
	Ele-	Freeze-	Oven-	Wet_	Dry
Samp1e	ment	dry	dry <sup>a</sup>	ash <sup>b</sup>	ash <sup>c</sup>
Cabbage or brine	Cr		X	X	
	Ni	X			X
Sauerkraut or brine	Cr		X	X	
	Ni	X			X
Honey	Cr			X	
	Ni			X	
Vinegar or wine	Cr		X	X	
	Ni		X	X	
Cheese whey	Cr			X	
	Ni_				X

a 110°C overnight

There are many factors which probably affect the release of such metals into acidic foods contacting stainless steel surfaces. These would include the metal area exposed, the pH of the food product, its temperature, time of contact, agitation, the specific stainless steel alloy and the presence of organic chelating constituents in the food. Citric acid is added to the red cabbage during processing. This organic acid is an excellent chelator which may be the reason Cr is high in the red cabbage brine. In addition, traces of these elements could be present in the food crops prior to processing, depending on the nature of the crop and the soil type and pH (BEAR 1955).

From a public health standpoint the concentrations of Cr and Ni found in the food products here probably do not constitute a hazard to consumers. The oral LD<sub>50</sub> values for chromic chloride and nickel nitrate (hexahydrate) for rats are 1870 and 1620 mg/kg, respectively, (CHRISTENSEN et al. 1976) which would place them in the category of low toxicity. Oral administration of soluble Cr salts to animals results in rapid and complete excretion (CONN et al. 1932). Nickel is also largely excreted following oral ingestion. Systemic toxic effects from this metal have rarely been observed even when therapeutic doses have been administered (BROWNING 1969). Indeed, recent research as reviewed by LISK (1972) indicates that Cr, especially in the trivalent form, and Ni may be essential elements.

b nitric acid-sulfuric acid-hydrogen peroxide (Anal. Methods Comm.)

c 500° C for 24 hours

TABLE 2
Concentrations of chromium and nickel in food samples.

			Cr		Ni	
		Sample	ppm		ppm	
Commodity	Container	T pH	wet wt.	dry wt.	wet wt.	dry wt.
Red cabbage Red cabbage brine	glass glass	3.4	2.6 10.3	52.8	0.29 1.1	5.7
Sauerkraut Sauerkraut brine	can can	3.5	0.3 0.3	6.1	0.02 0.01	0.3
Sauerkraut	flexible pouch		0.2	3.2	0.03	0.5
Sauerkraut brine	flexible pouch	3.5	0.2		0.02	
Honey No. 1	g1ass	3.7	0.15		0.08	
Honey No. 2	g1ass	3.7	0.13		0.03	
Honey No. 3	glass	3.7	0.04		0.08	
Honey No. 4	glass	3.5	0.18		0.03	
Honey No. 5	glass	3.5	0.11		0.03	
Honey (control)	direct from comb	4.2	0.02		0.08	
Vinegar	bulk .	2.8	0.01		0.05	
Hard cider	bulk <sup>2</sup>	3.5	0.004		0.04	
Cheese whey	bulk	4.8	0.01	0.1	0.04	0.8
Wine, Catawba	Lastiglas one year		0.02		0.03	
Wine, Red Concord	redwood, 8 mos.	3.2	0.07		0.04	
Wine, Red Concord	stainless steel, 7 mos.	3.2	0.02		0.04	
Seibel-9549	oak, 8 mos.	3.4	0.01		0.04	

<sup>1</sup> All commodities were commercial grade, except control honey.

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<sup>2</sup> Before acetification

#### REFERENCES

- ANALYTICAL METHODS COMMITTEE: Analyst 85, 643 (1960).
- BEAR, F. E.: 1955. Chemistry of the Soil. A. C. S. Monograph No. 126, Reinhold Publishing Corp., New York.
- BROWNING, E.: 1969. Toxicology of Industrial Metals. Butterworths, London, page 251.
- CARY, E. E. and W. H. ALLAWAY: J. Agric. Food Chem. 19, 1159 (1971).
- CARY, E. E. and O. E. OLSON: J. Assoc. Offic. Anal. Chemists <u>58</u>, 433 (1975).
- CHRISTENSEN, H. E., E. J. FAIRCHILD, B. S. CARROLL and R. J. LEWIS: 1976. Registry of Toxic Effects of Chemical Substances. U. S. Dept. Health, Education and Welfare, (National Institutes for Occupational Safety and Health,) Rockville, MD 20852.
- CONN, L. W., H. L. WEBSTER and A. H. JOHNSON: Amer. J. Hygiene 15, 760 (1932).
- LANGE, N. A.: 1949. Handbook of Chemistry. Handbook Publishers Inc., Sandusky, OH, 7th ed., page 819.
- LISK, D. J.: 1972. Trace Metals in Soils, Plants and Animals in Advances in Agronomy, Vol. 24, N. C. Brady, Ed., Academic Press, New York.
- TONG, S. S. C., R. A. MORSE, C. A. BACHE and D. J. LISK: Arch. Environ. Health 30, 329 (1975).
- ZACHARIASEN, H., I. ANDERSEN, C. KOSTOL and R. BARTON: Clinical Chemistry 21, 562 (1975).