Trace Metal and Protein Concentrations in California Market Milks

J. C. BRUHN\(^1\) and A. A. FRANKE\(^2\)

Cooperative Extension and Department of Food Science and Technology, University of California, Davis, California 95616

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**ABSTRACT**

Market milk samples (225) were collected in three major milk marketing areas in California. Samples represented four products: regular, extra-rich, non-fat, and low-fat milk. Concentrations of cadmium, copper, lead, zinc, and protein were measured in all samples. The concentration of selenium was measured in 103 of the samples. Mean concentrations in all samples examined were: cadmium 5.0; copper, 41.0; lead, 60.3; and selenium, 24.4 μg/kg. No significant differences between market or product means were found for these four metals. Mean product concentrations for protein and zinc were: regular milk, 3.29% protein and 3.61 mg/kg zinc; extra-rich milk, 3.33% and 3.70 mg/kg; non-fat milk, 3.61% and 3.98 mg/kg; and low-fat milk, 3.82% and 4.18 mg/kg. Low-fat and nonfat milks had significantly (\(p < 0.05\)) greater concentrations of protein and zinc than did regular and extra-rich milks.

Contamination of our food supply by environmental pollutants is receiving increased attention (4). Attention has been focused on milk, particularly since it is the principal food of infant nutrition and can provide a major part of human nutrition.

Surveys of California herd milk (4, 5) have established limiting and mean concentrations for copper, lead, and cadmium occurring in raw milk. The present survey of market milk was undertaken to determine what influences processing and product standardization would have on these trace elements.

The nutritionally important element zinc and protein were also determined in market milks. Selenium was also measured in some market milk because of the concern (9) expressed relating a selenium deficiency to the sudden infant death syndrome. Millar and Sheppard (8) have stated that the selenium concentration in cows' milk is significantly lower than in human milk. The importance of having background information on the selenium concentration in market milk was therefore warranted.

**MATERIALS AND METHODS**

Samples of four products: regular, extra-rich, non-fat, and low-fat milk, were collected from markets in the San Francisco Bay Area and Sacramento Valley (Northern California), and the Los Angeles Metropolitan Area (Southern California) and held at 4°C until analyzed.

### TABLE 1. Composition standards for California market milk

<table>
<thead>
<tr>
<th>Component</th>
<th>Non-fat</th>
<th>Low-fat</th>
<th>Regular</th>
<th>Extra-rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat</td>
<td>≥0.25</td>
<td>1.9-2.1</td>
<td>≥3.5</td>
<td>no standard(^a)</td>
</tr>
<tr>
<td>Solids not fat</td>
<td>&gt;9.0</td>
<td>≥10.0</td>
<td>&gt;8.7</td>
<td>no standard(^a)</td>
</tr>
</tbody>
</table>

\(^a\)Product must be clearly labelled "20% (or more) richer in than regular milk."

The California product standards are given in Table 1. Once the carton had been opened, all samples required for the different analyses were prepared as quickly as possible, generally within 4 h. The remaining milk was frozen and stored.

Copper determinations were made by the procedure reported previously (4) with no modification. Lead and cadmium determinations were made by the procedure reported previously (5) except that absorbance at 283 nm instead of 217 nm was used to quantify lead.

Zinc determinations were made by dry ashing 100-g samples, dissolving the ash in 15 ml of 2.4 N HCl, diluting the dissolved ash in 100 ml of double deionized water and aspirating the final solution into an atomic absorption spectrophotometer (1). Absorption measurements were made at 214 nm using an air-acetylene flame. Standards were prepared from a Fisher Certified 1000 ppm solution diluted with 0.36 N HCl to obtain concentrations in the range of 0.5 mg/kg (0.5 mg/kg increments). This procedure was tested for accuracy and precision before application to the samples. Recoveries of zinc added to milk in the range 0 to 1.25 mg/kg (0.25 mg/kg increments) averaged 98.91 ± 0.29% (mean ± standard deviation, six trials). The standard deviation of triplicate analyses ranged from 0.01 to 0.06 mg/kg.

Selenium determinations were made by the wet ashing—fluorometric procedure recommended by the Association of Official Analytical Chemists (7). Recoveries of selenium added to milk in the range 0 to 54 μg/l (9, 5, 18, and 50) averaged 99.14%, with a standard deviation of 1.84%.

Protein determinations were made by the dye-binding procedure recommended by the Association of Official Analytical Chemists (2). This procedure is a better test for total protein than Kjeldahl since the latter includes non-protein nitrogen (17). Our research using 21 herd milk samples collected in the Sacramento Valley indicates that the correlation coefficient (r) exceeds 0.99. The mean difference between triplicate determinations by dye binding and Kjeldahl was 0.014% protein.

Statistical analyses were done according to Snedecor and Cochran (15). Levels of significance are all reported at \(p = 0.05\).

**RESULTS AND DISCUSSION**

The results are summarized in Tables 2 and 3.

**Copper**

The mean copper concentration found in the 225 market milk samples was 41 μg/kg with a standard
TABLE 2. Mean concentrations of trace metals in California market milk

<table>
<thead>
<tr>
<th></th>
<th>Copper (µg/kg)</th>
<th>Lead (µg/kg)</th>
<th>Cadmium (µg/kg)</th>
<th>Selenium (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regular</td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
</tr>
<tr>
<td>N. Calif.</td>
<td>38.8 ± 0.08</td>
<td>3.29 ± 0.08</td>
<td>0.32 ± 0.12</td>
<td>15.6 ± 1.4</td>
</tr>
<tr>
<td>S. Calif.</td>
<td>39.5 ± 0.11</td>
<td>3.48 ± 0.11</td>
<td>0.34 ± 0.12</td>
<td>16.5 ± 1.5</td>
</tr>
<tr>
<td>Statewide</td>
<td>40.4 ± 0.12</td>
<td>3.55 ± 0.12</td>
<td>0.35 ± 0.12</td>
<td>17.5 ± 1.6</td>
</tr>
</tbody>
</table>

aSee Table 1 for product standards.

TABLE 3. Protein and zinc concentrations in California market milks

<table>
<thead>
<tr>
<th>Product</th>
<th>Protein</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regular milk</td>
<td>3.29 ± 0.08b</td>
<td>3.61 ± 0.3b</td>
</tr>
<tr>
<td>Extra-rich</td>
<td>3.33 ± 0.15</td>
<td>3.70 ± 0.35</td>
</tr>
<tr>
<td>Avg. R + X</td>
<td>3.31 ± 0.11</td>
<td>3.64 ± 0.33</td>
</tr>
<tr>
<td>Non-fat milk</td>
<td>3.61 ± 0.26</td>
<td>3.98 ± 0.37</td>
</tr>
<tr>
<td>Low-fat milk</td>
<td>3.82 ± 0.12</td>
<td>4.38 ± 0.31</td>
</tr>
<tr>
<td>Avg. N + L</td>
<td>3.71 ± 0.20</td>
<td>4.08 ± 0.34</td>
</tr>
<tr>
<td>Avg. all samples</td>
<td>3.52 ± 0.17</td>
<td>3.88 ± 0.34</td>
</tr>
</tbody>
</table>

aSee Table 1 for product standards.

bMean ± Standard deviation.

The mean copper concentration found in the 225 market milk samples was 32 µg/kg with a standard deviation of 32 µg/kg. The frequency distribution of concentrations found (Fig. 2) is skewed toward the lower concentrations, just as reported for raw milks (5). In the market milk samples, 50% had less than 55 µg lead/kg, and 95% had less than 156 µg lead/kg. There is very little probability that one would find a market milk in California containing as much as 156 µg/kg.

Data on lead concentration were examined for significant market and/or product differences. None were found. The difference between markets was consistent, however, Northern California samples averaging about 23 µg/kg higher than those collected in Southern California.

Our lead values are similar to those reported by Murthy et al. (10). Our range was from 5 to 183 µg/kg milk, while they reported a range from 19 to 104 µg/kg milk for samples collected in California during 1965 and 1966.

Cadmium

The mean cadmium concentration found in 225 market milk samples was 5 µg/kg with a standard deviation of 3 µg/kg. The frequency distribution of concentrations found (Fig. 3) is again skewed toward low concentration, just as it was for data collected for raw milk (5). The cadmium concentrations found in market milk are the same as reported in raw milk. Fifty percent of the samples had less than 5 µg/kg milk, and 95% of the samples had less than 10 µg/kg. There is very little...
probability that one would find a market milk in California containing more than 14 μg cadmium/kg. There were no significant differences between products or markets with respect to cadmium concentration.

Compared to data reported by Murthy and Rhea (11) the values reported here are significantly lower. Our range was from 1 to 17 μg/kg milk, while they reported a range from 17 to 30 μg/kg nationally.

Selenium

The mean selenium concentration found in 103 samples of market milk was 24 μg/l with a standard deviation of 11 μg/l. The frequency distribution of concentrations found (Fig. 4) appears rather random.

Among the samples studied, 50% had less than 19 μg/l and 95% had less than 39 μg/l. There is very little probability that one would find a market milk in California containing more than 57 μg/l.

We found values that ranged between 7 and 54 μg/l; Millar et al. (8) reported 2.9 to 9.7 μg/l in New Zealand milks, and Bisbjerg et al. (3) reported an average value of 23 μg/l for Danish milk. We found no significant differences between products or marketing areas, though the samples collected in Southern California averaged about 5 μg/l higher than those from Northern California. It is quite possible that real regional and seasonal differences exist since selenium might be associated with the protein in milk (6).

zinc concentrations found are complicated by the addition of non-fat dry milk solids to some of the extra-rich, non-fat, and low-fat milks. This is most apparent in the protein distribution, which is bimodal; there are two populations here, one centered about the mean value for regular and extra-rich milks, the other about the mean value for non-fat and low-fat milks. This is not so apparent for zinc because the zinc concentrations in each product are so variable.

Parkesh and Jenness (13) reported that about 88% of the zinc in milk is associated with the casein, so the relationship between zinc and protein concentrations found in California market milks is not surprising. The regular increase in zinc and protein concentrations from regular to low-fat milk is a consequence of the solids not fat standards for these products (Table 4). Non-fat and low-fat milk have significantly higher concentrations of zinc and protein than do regular and extra-rich milks, so a discussion of the probability of maximum or minimum values must be related to each individual product. Since the minimum value is more important nutritionally both

**Figure 3.** Frequency distribution of cadmium concentrations in California market milk.

**Figure 4.** Frequency distribution of selenium concentrations in California market milk.

**Figure 5.** Frequency distribution of protein concentrations in California market milk.

**Figure 6.** Frequency distribution of zinc concentrations in California market milk.
TABLE 4. The effect of product standardization for solids not fat on the concentrations of zinc and protein in the products

<table>
<thead>
<tr>
<th>Component</th>
<th>Product</th>
<th>Regular</th>
<th>Extra-rich</th>
<th>Non-fat</th>
<th>Low-fat</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNF, %a</td>
<td></td>
<td>8.7</td>
<td>9.0</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>Zinc, mg/kgb</td>
<td></td>
<td>3.61</td>
<td>3.70</td>
<td>3.98</td>
<td>4.18</td>
</tr>
<tr>
<td>Protein, %b</td>
<td></td>
<td>3.29</td>
<td>3.33</td>
<td>3.61</td>
<td>3.82</td>
</tr>
</tbody>
</table>

a State requirements.

b Differences between means sharing the same underline are not significant, a = .05.

For protein and zinc, we can state that the minimum concentrations of protein and zinc likely to be encountered by the California consumer are in regular milk, and are 3.05 g of protein/100 g and 2.45 mg of zinc/kg. So a 100 g serving of regular milk provides at least 5.4% of the RDA for protein and 1.0% of the RDA for zinc.

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REFERENCES


