Analysis of Milk Powder by Direct Nebulization into Inductively-coupled Plasma

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Key words: ICP; nebulization; suspensions; infant milk powder; analysis.

ABSTRACT

Sample preparation has always been a tedious but important step in analysis involving Inductively Coupled plasma emission spectrometry. In addition, it may also be a source of sample contamination. The present work attempts to overcome these problems by nebulizing milk powder suspensions directly into the plasma. Various infant and full cream milk powders were dispersed in water as well as 0.5% triton-X solution. The suspensions were then analysed for calcium, phosphorus, iron, magnesium and sodium. These elements were successfully determined using inorganic standards with the addition of an internal standard to correct for the difference in viscosities.

INTRODUCTION

The use of inductively coupled plasma atomic emission spectrometry to detect both metallic and non-metallic elements in a variety of sample matrices has been well documented. However, a disadvantage is that it requires the sample to be in solution. This is usually time consuming, increases the opportunities for sample contamination and/or loss of sample constituents. In order to eliminate these problems, a more recent trend has been toward the direct introduction of solid samples into the plasma. The methods proposed include direct sample insertion (Zhang et al., 1983; Kirkbright and Walton, 1982), electrothermal carbon cup sample vaporization (Ng and Caruso, 1983), sample elevator technique using a high power ICP (Sommer and Ohls, 1980), spark elutriation of powders into ICP (Scott, 1978), laser ablation (Thompson et al., 1981) and slurry nebulization (Wilkinson et al., 1982; Sugimae et al., 1982; Schramel, 1979).

Gunn et al. (1977) reported the determination of phosphorus in milk powders using a

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1 A modified version of the paper has been presented at the Asian Chemical Conference, 1985 in Singapore.

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high frequency inductively-coupled argon plasma source. A solution of milk powder in acetic acid was prepared; pneumatic nebulization of the aqueous solution yielded results with a relative standard deviation of 2%. They showed that phosphorus in milk powder solution could be analyzed relatively easily and accurately. Schramel (1979) determined boron and certain other metals in milk using an ultrasonic nebulizer and found the results acceptable. In this paper, we describe a rapid and convenient method in which the major elements in various milk powders are determined by direct nebulization of suspensions into the inductively-coupled plasma source.

MATERIALS AND METHODS

The Inductively Coupled Plasma Atomic Emission Spectrometer (ICPAES) used was a commercially available Labtest Model 2000. The instrumentation and operating conditions are listed in Table 1.

A stop-flow nebulizer operating on Babbage’s principle (Moore et al., 1984) was used. It has great potential for the introduction of liquids with high percentages of dissolved and suspended solids. The computer programme allows for a sweep of argon gas in between analysis to eliminate crystal formation at the gas-liquid interface.

Ca, Fe, Mg, Na and P were analysed at emission lines of 317.9, 259.9, 279.5, 588.9 and 178.2 nm respectively.

Reagents and Materials

All chemicals used were of analytical reagent grade from BDH Chemicals Ltd. All stock solutions and dilutions were prepared with 2% aqua regia prepared from redistilled acids.

Analysed milk powder samples were kindly supplied by Wyeth Pharmaceuticals Pty. Ltd. and Nestle Regional Laboratory, New South Wales, Australia.

Procedure

For dry ashing, 3.2 g of the milk powder was weighed accurately in duplicate, heated on a hot plate till charred and ashed in a furnace at 450°C for 16 hours. The resulting ash was then dissolved in 2% aqua regia and made up to 25 cm³.

TABLE 1
ICP instrumentation and operating conditions

<table>
<thead>
<tr>
<th>Instrumentation</th>
<th>Labtest Model 2000, 0.4 — 2kW, 27.12 MHz.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrometer</td>
<td>Labtest V25 vacuum spectrometer, 21 channels.</td>
</tr>
<tr>
<td>Detector</td>
<td>Simultaneous A/D conversions of all 21 phototube signals and data processing performed in Labtest 3000 multi-processor micro computer system</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>Labtest stop-flow GMK nebulizer, sample flow rate 1.5 cm³ min⁻¹</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plasma Operating Conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Forward power</td>
<td>1400 W</td>
</tr>
<tr>
<td>Reflected power</td>
<td>5 W</td>
</tr>
<tr>
<td>Spectrometer slits</td>
<td>20 μm entrance, 50 — 70 μm exit slits</td>
</tr>
<tr>
<td>Argon coolant flow rate</td>
<td>14.0 dm³ min⁻¹</td>
</tr>
<tr>
<td>Argon carrier flow rate</td>
<td>0.9 dm³ min⁻¹</td>
</tr>
<tr>
<td>Viewing height</td>
<td>14 mm above coil</td>
</tr>
</tbody>
</table>
To prepare milk suspensions, 6.4 g milk powder was weighed accurately and dispersed in either distilled water or 0.5% Triton-X solution and made up to 50 cm$^3$. This gives reformulation of 128 g milk powder per dm$^3$ solution which is the strength for feeding infants recommended by the manufacturer. A ten-fold diluted formulation was prepared by dispersing 0.64 g milk powder in either distilled water or 0.5% Triton-X solution. All milk suspensions were prepared in duplicates. Milk suspensions thus prepared were found to be stable for more than a week when kept at 4°C. They were analysed for calcium, iron, magnesium, sodium and phosphorus on the ICP emission spectrometer using (i) a milk suspension as calibration standard, and (ii) inorganic standards with chromium as an internal standard for calibration. Two inorganic standards were used. The mixed high inorganic standard was made up of 400 ppm Ca, 300 ppm P, 200 ppm Na, 40 ppm Mg, 10 ppm Fe and 20 ppm Cr as internal standard. The mixed low inorganic standard was a ten-fold dilution of the high standard, retaining Cr at 20 ppm. These standards were made up in 2% aqua regia.

RESULTS AND DISCUSSION

Choice of Dispersant and Concentration of Milk Powder

Dispersion of the specially formulated infant milk powder in water and in 0.5% Triton-X solution does not seem to produce any difference in the analytical results as shown in Table 2. However, Triton-X solution was preferred as milk powder dispersed more readily in it and this medium prevented adhesion of particles on to the walls of the tubings.

In the case of the ordinary infant milk powder and full cream milk powder, dispersion in water appeared to give slightly lower results than dispersion in Triton-X solution as shown in Table 3. This could be due to the higher fat content in the milk powder which rendered its dispersion in water less uniform.

Milk suspensions prepared based on the reformulation formula recommended by the manufacturer 128 g dm$^{-3}$ did not differ from milk suspensions which were ten-fold diluted in their analyses as shown in Tables 2 and 3. In the study of direct aspiration of coal slurries into the ICP using a similar nebulizer, Wilkinson et al. (1982) found that linearity was obtained for slurry concentrations up to approximately 20% w/v in 0.5% Triton-X solution in the manganese emission signal. In the present study, the slurry concentrations are 1.28% and 12.8% (w/v) in water as well as in 0.5% Triton-X solution, thus it is not unexpected that the linearity of the elemental emission signals was observed. The choice of the ten-fold diluted formula was based on physical observation. The time required to produce a uniformly dispersed milk suspension was longer for the more concentrated formulation and the plasma showed some instabilities, like fluctuations of the reflected power when the suspension was nebulized.

Choice of Standards

The compositions of the milk powders studied were determined by the dry ashing method. Five different batches of the specially formulated infant milk powder were obtained and the dry ashing determinations agreed well with the manufacturer's specifications as shown in Table 2.

In order to have close matching of sample suspensions and standard suspensions with respect to chemical and particle size composition, one of the samples was used as a calibration standard for the analysis of the other samples. Results are shown in Table 2. There is a good agreement between these results and those obtained after dry ashing.

Assuming that the main difference between a milk suspension and an aqueous solution is that of the problem of transport arising from their differences in particle size composition, the use of an internal standard should correct for the discrepancies. The milk suspensions were thus analysed using mixed inorganic standards with Cr as an internal standard. The results in Table
TABLE 2
Comparison of various analytical methods for a special infant milk powder
Concentration of elements (mg dm⁻³) based on reformulation of 128 g milk powder per dm⁻³ solution

<table>
<thead>
<tr>
<th>Analytical method</th>
<th>Ca Sample A B C D E</th>
<th>Fe Sample A B C D E</th>
<th>Mg Sample A B C D E</th>
<th>Na Sample A B C D E</th>
<th>P Sample A B C D E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low temp. ash, aqueous nebulization</td>
<td>439 439 472 470 462</td>
<td>13.7 13.9 13.9 13.7 13.4</td>
<td>49.5 48.5 51.5 51.5 52.5</td>
<td>126 145 131 129 127</td>
<td>308 308 315 321 313</td>
</tr>
<tr>
<td>Manufactures' specification</td>
<td>444</td>
<td>12.7</td>
<td>53</td>
<td>150</td>
<td>330</td>
</tr>
<tr>
<td>Slurry nebulization</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) Milk suspension (D) as calibration standard</td>
<td>443 454 459 459 454</td>
<td>13.1 13.3 13.4 13.3</td>
<td>48.8 49.9 50.5 51.5</td>
<td>123 126 127 131</td>
<td>305 316 314 315</td>
</tr>
<tr>
<td>b) Mixed aqueous low inorganic std. as calibration std.</td>
<td>459 459 458 471 455</td>
<td>13.0 12.9 13.0 13.3 12.6</td>
<td>49.8 49.8 50.2 51.5 51.1</td>
<td>122 128 122 129 120</td>
<td>317 325 318 325 319</td>
</tr>
<tr>
<td>c) Mixed aqueous high inorganic std. as calibration std.</td>
<td>440 447 446 460 444 462*</td>
<td>12.8 13.0 13.0 13.1 13.0</td>
<td>49.0 50.1 49.9 51.2 50.7</td>
<td>129 130 130 130 135</td>
<td>309 308 315 316 314</td>
</tr>
<tr>
<td>d) Mixed high inorganic standard in 0.5% T-X</td>
<td>443 452 447 457 444 **465 464 474 476 455</td>
<td>12.3 12.9 12.4 12.8 13.3</td>
<td>51.5 50.7 52.4 51.0 51.4</td>
<td>137 136 132 131 123</td>
<td>357 357 358 341* 339</td>
</tr>
<tr>
<td>RSD for replicate preparations</td>
<td>1.05%</td>
<td>0.56%</td>
<td>0.71%</td>
<td>1.52%</td>
<td>1.30%</td>
</tr>
<tr>
<td>RSD for 10 integrations for each sample preparation</td>
<td>&lt;1.05%</td>
<td>&lt;2.5%</td>
<td>&lt;1.0%</td>
<td>&lt;2.5%</td>
<td>&lt;3.0%</td>
</tr>
</tbody>
</table>

Sample A, B, C, D and E are five different batches of the infant milk powder.
*The milk powder was dispersed in water.
**Concentration of milk suspensions was 6.4 in 50 cm⁻³ Triton-X solution.
### TABLE 3
Comparison of various analytical methods for ordinary infant milk powder, infant soy and full cream milk powder
Concentration of elements (mg dm$^{-3}$) based on reformulation of 128 g milk powder per dm$^3$ solution

<table>
<thead>
<tr>
<th>Analytical Method</th>
<th>Ca</th>
<th>Fe</th>
<th>Mg</th>
<th>Na</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Infant</td>
<td>Infant</td>
<td>Full</td>
<td>Infant</td>
<td>Infant</td>
</tr>
<tr>
<td></td>
<td>$F$</td>
<td>$G$</td>
<td>$F$</td>
<td>$G$</td>
<td>$F$</td>
</tr>
<tr>
<td>Low temp. ash, aqueous nebulization</td>
<td>726</td>
<td>702</td>
<td>565</td>
<td>1157</td>
<td>-</td>
</tr>
<tr>
<td>Slurry nebulization</td>
<td>760</td>
<td>706</td>
<td>557</td>
<td>1223</td>
<td>-</td>
</tr>
<tr>
<td>Mixed aqueous low inorganic std. as calibration std.</td>
<td>760</td>
<td>706</td>
<td>557</td>
<td>1223</td>
<td>-</td>
</tr>
<tr>
<td>Mixed high inorganic Std in 0.5% T-X</td>
<td>759</td>
<td>1225</td>
<td>8.8</td>
<td>-</td>
<td>77.8</td>
</tr>
</tbody>
</table>

**RSD for 10 integrations for each sample preparation**

- $<1.0\%$
- $<2.0\%$
- $<1.0\%$
- $<2.0\%$
- $<2.5\%$

$F$, $G$ are two different batches of the ordinary infant milk powder.

*The milk powder was dispersed in water.

**Concentration of milk suspensions was 6.4 g in 50 cm$^3$ Triton-X solution.
2 showed that this could indeed overcome the problem.

As the milk suspensions were prepared in 0.5% Triton-X solution, an inorganic standard prepared in 0.5% Triton-X solution was used to see if there could be any improvement in the analytical results. There were, however, no great differences. The simplest and most direct method of analysis is, therefore, to use an inorganic standard with an internal standard and direct nebulization of the milk suspensions prepared in 0.5% Triton-X solution.

Analysis of Milk Powders

In addition to the specially formulated milk powders, an infant soybean substitute for milk, an ordinary infant milk powder and a full cream milk powder were analysed using slurry nebulization. The results in Table 3 show these agreed well with the determinations obtained by slurry nebulizations and aqueous nebulization of samples after dry ashing.

The precision of the method was estimated by carrying out replicate analyses of the five batches of specially formulated infant milk powders. Two separate suspensions were prepared for each batch of the milk powder and ten replicate analyses were then made on each of these solutions. The average relative standard deviations are shown in Table 2. The relative standard deviations for replicate preparations for all the elements were less than 2%. Replicate analyses on each solution yield relative standard deviation of < 1.0% to < 3.0%, varying from element to element.

ACKNOWLEDGEMENT

The authors would like to express their thanks to the Australian Universities International Development Programme (AUIDP) for making possible C.K. Lee’s visit to the Universiti of New South Wales and for financing the research project.

REFERENCES


(Received 7 February, 1986)