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Analysis of Milk Powder by Direct Nebulization into Inductively-coupled Plasma [1]

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ABSTRAK

Penyediaan sampel memakan masa tetapi perlu dalam analisis yang melibatkan spektrometri pancaran Plasma Gandingan Aruhan. Sebagai tambahan, ia juga merupakan sumber bagi cemaran sampel. Kajian ini cuba mengatasi masalah ini dengan memasukkan ampaian susu tepung terus ke dalam plasma. Beberapa jenis susu tepung bayi dan penuh-krim diampaikan dalam air dan juga 0.5% larutan Triton-X. Ampaian-ampaian ini dianalisis untuk mengetahui kandungan kalsium, fosforus, besi, magnesium dan natrium. Unsur-unsur ini telah ditentukan dengan menggunakan piawaian tak organik dengan tambahan satu piawai dalaman untuk mengatasi perbezaan kelikatan.

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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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 Babington 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 cm^3.

TABLE 1
ICP instrumentation and operating conditions

Instrumentation	
Plasma power supply	Labtest Model 2000, 0.4 – 2kW, 27.12 MHz.
Spectrometer	Labtest V25 vacuum spectrometer, 21 channels.
Detector	Simultaneous A/D conversions of all 21 phototube signals and data processing performed in Labtest 3000 multi-processor micro computer system
Nebulizer	Labtest stop-flow GMK nebulizer, sample flow rate 1.5 $cm^3 min^{-1}$.
Plasma Operating Conditions	
Forward power	1400 W
Reflected power	5 W
Spectrometer slits	20 μm entrance, 50 – 70 μm exit slits
Argon coolent flow rate	14.0 $dm^3 min^{-1}$
Argon carrier flow rate	0.9 $dm^3 min^{-1}$
Viewing height	14 mm above coil

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 adhersion 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

Analytical method	Ca Sample					Fe Sample					Mg Sample					Na Sample					P Sample				
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
Low temp. ash, aqueous nebulization	439	439	472	470	462	13.7	13.9	13.9	13.7	13.4	49.5	48.5	51.5	51.5	52.5	126	145	131	129	127	308	308	315	321	313
Manufactures' specification			444					12.7					53					150					330		
Slurry nebulization																									
a) Milk suspension (D) as calibration standard	443	454	459	–	454	13.1	13.3	13.4	–	13.3	48.8	49.9	50.5	–	51.5	123	126	127	–	131	305	316	314	–	315
b) Mixed aqueous low inorganic std. as calibration std.	459	454	458	471	455	13.0	12.9	13.0	13.3	12.6	49.8	49.8	50.2	51.5	51.1	122	128	122	129	120	317	325	318	325	319
				459*					13.0					48.9*					128*						
c) Mixed aqueous high inorganic std. as calibration std.	440	447	446	460	444	12.8	13.0	13.0	13.1	13.0	49.0	50.1	49.9	51.2	50.7	129	130	130	130	135	309	308	315	316	314
				462*																					
	**465	464	474	476	455	12.3	12.9	12.4	12.8	13.3	51.5	50.7	52.4	51.0*	51.4	137	136	132	131*	123	357	357	358	341*	339
d) Mixed high inorganic standard in 0.5% T-X	443	452	447	457	444	12.4	12.6	12.2	12.9	12.2	49.5	50.1	49.8	50.5	50.7	117	122	113	129	121	288	299	289	316	292
RSD for replicate preparations		1.05%						0.56%					0.71%					1.52%					1.30%		
RSD for 10 integrations for each sample preparation		<1.05%						<2.5%					<1.0%					<2.5%					<3.0%		

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

	Analytical Method	Ca				Fe				Mg				Na				P			
		Infant		Infant soy	Full cream	Infant		Infant soy	Full cream	Infant		Infant soy	Full cream	Infant		Infant soy	Full cream	Infant		Infant soy	Full cream
		F	G			F	G			F	G			F	G			F	G		
	Low temp. ash, aqueous nebulization	726	702	565	1157	8.7	9.4	12.6	—	72.4	68.5	66.5	116	297	273	305	477	554	518	443	924
	Slurry nebulization																				
a)	Mixed aqueous low inorganic std. as calibration std.	760	706	557	1223	8.8	9.2	9.0	—	76.7	71.8	65.5	120	299	277	273	471	589	540	400	945
		724*			1188*	8.9*				72.5*				277*			446*	547*			910*
b)	Mixed aqueous high inorganic std. as calibration std.	760	700	549	1225	8.3	9.1	9.8	—	77.8	72.1	65.8	126	305	280	285	476	589	516	382	945
		743*			1206*	8.8				74.9*			129*	300*			472*	603*			1012*
		**745	695			9.3	9.8			76.4	69.0			291	268			613	567		
c)	Mixed high inorganic Std in 0.5% T-X	759			1225	8.8			—	77.8			126	288			473	575			960
	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.

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