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## Determination of Copper, Cobalt, Nickel, and Manganese in Baby Food Slurries Using Electrothermal Atomic Absorption Spectrometry

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The analytical conditions for the electrothermal atomic absorption spectrometric determination of copper, manganese, nickel, and cobalt in different types of baby foods using slurried samples are presented. Suspensions were prepared in a medium containing 0.1% w/v Triton X-100, 30% v/v concentrated hydrogen peroxide, 1% v/v concentrated nitric acid, 1% w/v ammonium dihydrogenphosphate (only for copper atomization), and one drop of silicon antifoam. The slurries were homogenized by using a potter and were introduced directly into the furnace. The amount of analyte extracted to the liquid phase was investigated. The graphite furnace conditions were optimized for each element. No matrix effect was observed, and calibration could be carried out using aqueous standard solutions. The detection limits were 3.4, 2.1, 5.4, and 3.7 pg for copper, manganese, nickel, and cobalt, respectively. The reliability of the procedures was checked by statistically comparing the results obtained with those found by using a previous microwave-oven mineralization stage and by analyzing several certified reference materials.

**Keywords:** *Electrothermal atomic absorption spectrometry; slurry sampling; copper; cobalt; nickel; manganese; baby foods*

### INTRODUCTION

In light of recent interest in the possible role which metals play in health problems and the limited data available on trace element concentrations in baby foods, a multielement survey of baby foods (Ministry of Agriculture, Fisheries and Food, 1995) has been published to establish infant exposure to several elements from the diet. Copper, cobalt, nickel, and manganese are elements considered as essential nutrients. An average single day's diet may contain 10 mg or more copper, which is distributed throughout the body (Seiler et al., 1994). Cobalt is present in green vegetables and animal food; animals are able to synthesize vitamin B<sub>12</sub>, which

is the main source of Co. Generally, in humans the oral intake of nickel is derived primarily from food, where concentrations are usually below 0.5 mg/kg fresh weight. Although a relatively common metal in the biosphere, manganese does not usually occur in large amounts in plant materials. However, it is an essential nutrient for most living organisms and it is present in small amounts in most living tissue (Seiler et al., 1994).

The prime concerns when determining the concentration of these oligoelements in foods are contamination and loss. Potential sources of contamination in the laboratory include impurities in the reagents or in the laboratory apparatus used and the dust. Consequently, particular attention should be given to the collection and treatment of the sample prior to analysis. The most useful technique for these determinations is electrothermal atomic absorption spectrometry (ETAAS) since solid

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**Table 1. Instrumental Settings and Characteristics of the Recommended Procedures<sup>a</sup>**

parameter	element			
	copper	cobalt	nickel	manganese
wavelength (nm)	324.8	240.7	232.0	279.5
bandpass, (nm)	0.7	0.7	0.7	0.2
atomizer type	wall	wall	wall	platform
injection volume, ( $\mu$ L)	20	20	20	20
calibration, (ng/mL)	0–20	0–40	0–50	0–20
characteristic mass, (pg)	6.6	17	27	3.8
detection limit, (pg)	10	18	31	1.6

<sup>a</sup> The spectrometer used was a Perkin-Elmer Model 1100B equipped with deuterium-arc background correction and an HGA-400 graphite furnace atomizer.

and semisolid samples can be analyzed with minimal manipulation.

The introduction of solid samples in ETAAS has practical advantages over time-consuming conventional procedures based on total dissolution of the samples (Bendicho and de Loos-Vollebregt, 1991). Several ETAAS procedures using the slurry-based approach have been reported for copper, cobalt, nickel, and manganese determinations in foods (Stephen et al., 1987; Miller-Ihli, 1988; Jordan et al., 1989; Ebdon et al., 1990; Dobrowolski and Mierzwa, 1993; Hoening and Cilissen, 1993; Viñas et al., 1993; Viñas et al., 1994; Cabrera et al., 1995; Viñas et al., 1995; Tan et al., 1996; Carlosena et al., 1997; Meeravali and Kumar, 1998). However, the direct introduction of suspensions has certain drawbacks caused by high background values or the build-up of carbonaceous residues, which results in nonreproducible sample deposition and even partial obstruction of the light beam. These problems can be reduced by including an air-ashing step in the heating cycle (Ebdon et al., 1990). An alternative is the addition of both hydrogen peroxide and nitric acid to samples rich in organic carbon, which decreases the deposition of carbonaceous residues and does not damage the graphite tube atomizer (López-García et al., 1996; Viñas et al., 1994, 1995, 1999a).

In previous studies, we analyzed baby food samples to determine the contents of arsenic (Viñas et al., 1999b), selenium, lead, and cadmium (Viñas et al., 2000). In this paper, we report the results obtained from the application of this hydrogen peroxide-based methodology to the quantitation of copper, cobalt, nickel, and manganese in baby foods, which were directly introduced into the atomizer as slurries to minimize sample preparation. All the baby foods analyzed were in the form of purée. The reliability of the procedure was checked by dissolving the samples using a closed system and by analyzing several standard certified reference materials.

## EXPERIMENTAL PROCEDURES

**Instrumentation.** A Perkin-Elmer model 1100B atomic absorption spectrometer equipped with deuterium-arc background correction and an HGA-400 (Perkin-Elmer) graphite furnace atomizer were used. Pyrolytic graphite platforms (ref B012-1092) and pyrolytically coated graphite tubes (ref B013-5653) were obtained from Perkin-Elmer. Measurements were performed using hollow cathode lamps operated at the wavelengths and slit-widths given in Table 1. Platform atomization was used for manganese and wall atomization for copper, cobalt, and nickel. Argon was used as the inert gas, the flow rate being 300 mL/min during all the stages except for atomization, when the flow was stopped. Background-corrected integrated absorbance was used in all cases as the analytical signal.

**Table 2. Furnace Heating Programs<sup>a</sup>**

step	parameter	element			
		copper	cobalt	nickel	manganese
dry	<i>t</i> , °C	110	110	110	200
	ramp, s	10	10	10	15
	hold, s	60	60	60	60
calcination	<i>t</i> , °C	1100	1200	1000	NO
	ramp, s	1	1	1	
	hold, s	20	30	30	
cool	<i>t</i> , °C	20	20	20	NO
	ramp, s	1	1	1	
	hold, s	15	15	15	
atomization <sup>b</sup>	<i>t</i> , °C	1800	2600	2600	2000
	ramp, s	0	0	0	0
	hold, s	3	3	3	5
clean	<i>t</i> , °C	2650	2650	2650	2650
	ramp, s	1	1	1	1
	hold, s	3	3	3	3

<sup>a</sup> The spectrometer used was a Perkin-Elmer model 1100B equipped with deuterium-arc background correction and an HGA-400 graphite furnace atomizer. <sup>b</sup> The flow of argon was stopped during the atomization step.

Manual homogenization glass vessels (Potter, 10 mL) equipped with Teflon plungers were used. A Branson ultrasonic bath of 55 KHz and 14-W constant power was also used.

To decrease the risk of contamination, the use of glassware was reduced to a minimum, and plastic (polypropylene) vessels of the type commonly used to collect clinical samples were used for preparing and storing the solutions or suspensions. Pipet tips were also of polypropylene. All the glassware and plasticware was nitric acid-washed and rinsed with ultrapure water.

Mineralization of the samples for comparison purposes was carried out in closed Teflon cups using a MLS-1200 MEGA microwave oven (Milestone) and a MDR-1000/6 rotor (Radiometer).

**Reagents.** High quality water, obtained using a Milli-Q system (Millipore), was used exclusively. Copper, cobalt, nickel, and manganese standard solutions (1000  $\mu$ g/mL) were obtained from Panreac (Spain) and diluted as necessary to obtain working standards. Concentrated (65% w/v) nitric acid (E. M. Merck), 30% w/v hydrogen peroxide (Fluka), Triton X-100 (Merck), 30% w/v aqueous emulsion of antifoam A concentrate 100% active silicone polymer (Sigma), and ammonium dihydrogenphosphate (Fluka) were also used.

**Reference Materials and Samples.** To assess the reliability of the procedures, six reference materials were used. Total diet (HDP) sample was supplied by the Agricultural Research Centre of Finland (ARC/CL), whereas oyster tissue (SRM 1566a), bovine liver (SRM 1577b), rice flour (SRM 1568a), apple leaves (SRM 1515), and citrus leaves (SRM 1572) were supplied by the National Institute of Standards and Technology, NIST (USA). Various samples of purée baby food were purchased from several local supermarkets.

**Procedures.** The baby food samples were shaken manually before analysis. The suspensions were prepared by weighing the samples (the weight depended on the analyte and its level in the sample) directly into a Potter maceration tube and diluted with 5 mL of a solution containing 0.1% w/v Triton X-100, 1% v/v nitric acid, 30% v/v hydrogen peroxide, 1% w/v ammonium dihydrogenphosphate (only for copper atomization), and one drop of silicon antifoam. The slurries were homogenized by repeated movements of the plunger. It was verified that about 20 slow movements of the plunger, which took about 5 min, were sufficient to obtain a quasi-stable suspension. The suspensions were also sonicated for a few minutes to ensure the absence of lumps and sampled while they were being continuously stirred with a magnetic stirrer. Aliquots of 20  $\mu$ L were injected into the furnace. The heating program given in Table 2 (where the quoted temperatures are values set on the HGA-400 power supply) was run and the background-corrected peak areas due to the analyte were

obtained. Calibration was performed using aqueous standards. Certified reference samples were treated in the same way.

To confirm the reliability of the suspension-based procedures, the samples were mineralized by microwave oven treatment. For this, fractions (1–2 g) were weighed into Teflon cups and 3 mL of concentrated nitric acid and 0.5 mL of concentrated hydrogen peroxide were added. The program used in the microwave oven was that recommended by the manufacturer in the case of food samples with a water content higher than 60%. The program consisted of 1 min at 250 W, 1 min with no power applied, 6 min at 250 W, 6 min at 400 W, 4.5 min at 600 W, and 1.5 min at 250 W. After this treatment, the solutions were maintained in the closed cups for 10 min before being diluted with water up to 10 mL in volumetric flasks. These solutions were also analyzed by ETAAS using the same experimental conditions indicated for the suspensions.

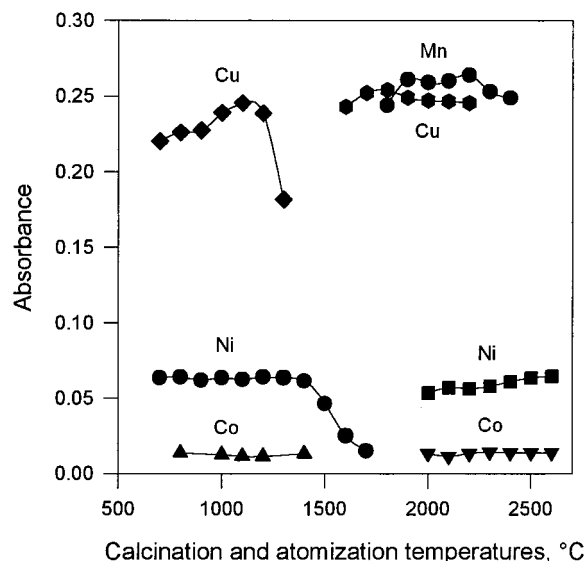
## RESULTS AND DISCUSSION

It was necessary to add a thixotropic thickening agent to achieve a stable suspension, and 0.1% w/v Triton X-100 and one drop of a silicone antifoam were added to avoid the formation of agglomerates in the suspension medium of the baby food samples, thus achieving reproducible sampling by micropipet.

### Optimization of the Furnace Heating Programs.

Conventional ETAAS methodology requires consecutive drying, ashing, and atomization steps. However, Halls (1984) demonstrated that the drying and ashing steps can be replaced by a modified drying step, thus shortening the furnace program time. Preliminary experiments were carried out using this fast-program methodology. For manganese, using a 1.5% w/v baby food suspension, liquid sputtering was noted at drying temperatures higher than 200 °C and when using a 1-s ramp time. It was therefore necessary to increase the drying time to ensure that the gas had completely removed the smoke before the atomization step. Consequently, drying was achieved with good reproducibility at 200 °C with a ramp of 15 s and a holding time of 60 s. The atomization temperature was varied between 1800 and 2400 °C and the maximum signal was reached above 1900 °C (Figure 1). Thus, the temperature selected was 2000 °C, which provided low background signals, thus permitting analysis without an ashing stage.

However, the atomization of nickel, cobalt, or copper required the injection of highly concentrated suspensions due to the low levels of these analytes in the baby food samples. Then, excessively high background values caused overcompensation effects, the ashing step could not be omitted, and it was necessary to use conventional heating programs. The optimal value for the drying temperature was 110 °C with a 10-s ramp to avoid sputtering and a 60-s holding time so that the samples were completely dry before calcination. Figure 1 shows the variation of the analytical signals for nickel, cobalt, and copper from different baby food suspensions when both the calcination and the atomization temperatures were varied. For nickel, using a 10% w/v baby food suspension, the calcination temperature was varied in the 700–1700 °C range and the analytical signal was constant up to 1300 °C; low background signals were obtained at 1000 °C and this value was selected. The atomization temperature was varied between 2000 and 2600 °C and this higher temperature was chosen because it provided the maximum signal. For cobalt, using a 20% w/v baby food suspension, the calcination temperature selected was 1200 °C to achieve lower



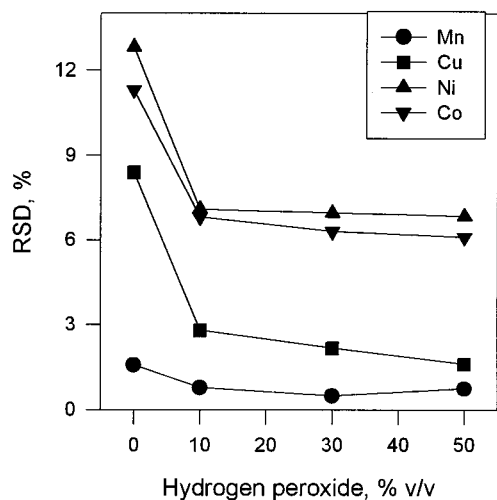
**Figure 1.** Influence of the calcination and atomization temperatures on the analytical signals for a baby food suspension containing 0.1% w/v Triton X-100, 30% v/v hydrogen peroxide, and 1% v/v nitric acid. Concentrations of the baby food samples were 1.5% w/v for manganese, 10% w/v for nickel, 20% w/v for cobalt, and 7% w/v for copper.

background signals when injecting the very concentrated suspensions necessary to obtain measurable analytical signals. The atomization temperature which gave the maximum signal was also 2600 °C. Finally, optimization of the heating program for copper was carried out using a 7% w/v baby food suspension; the calcination temperature selected was 1100 °C to avoid losses in the atomization of aqueous standards, while the atomization temperature giving a maximum signal was 1800 °C.

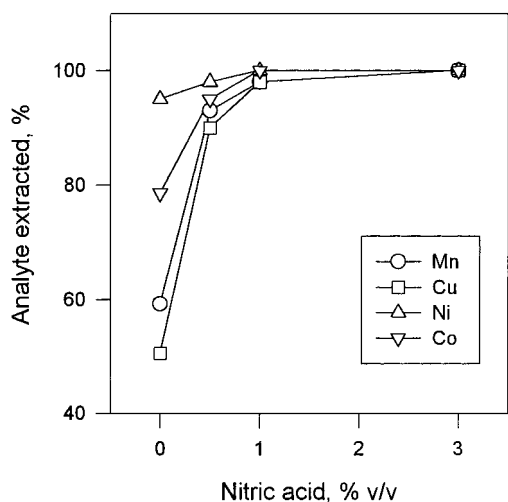
When using the atomization temperatures which provided maximum sensitivity, the atomization profiles appeared very quickly in nonisothermal conditions. Consequently, a cool step was also included in the heating programs for nickel, cobalt, and copper in order to delay the signals. This step consisted of a 1-s ramp at 20 °C with a 15-s holding time. A cleaning stage was also included in the heating cycle.

**Optimization of the Concentrations of the Chemical Agents.** The use of some chemical modifiers was studied. For manganese, the effect of adding ammonium dihydrogenphosphate was tested by varying its concentration in the 0.1–2.0% w/v range. No variation in the time of appearance of the analytical profile was observed over the whole range studied for either a 1.5% w/v baby food suspension or an aqueous standard. Similar results were obtained for the atomization of nickel and cobalt when using ammonium dihydrogenphosphate or magnesium nitrate as modifiers. Consequently, the atomization of manganese, nickel, and cobalt did not require any modifier. For copper, a slight delay in the atomization profile was observed in the presence of 1% w/v ammonium dihydrogenphosphate and so this modifier was used.

The presence of hydrogen peroxide has an important effect on the elimination of carbonaceous residues in the atomizer (López-García et al., 1996; Viñas et al., 1995, 1999a,b, 2000). When the concentration of this chemical was varied in the 0–50% v/v range, no significant changes in the analytical signals or in the background were noted, although the relative standard deviation



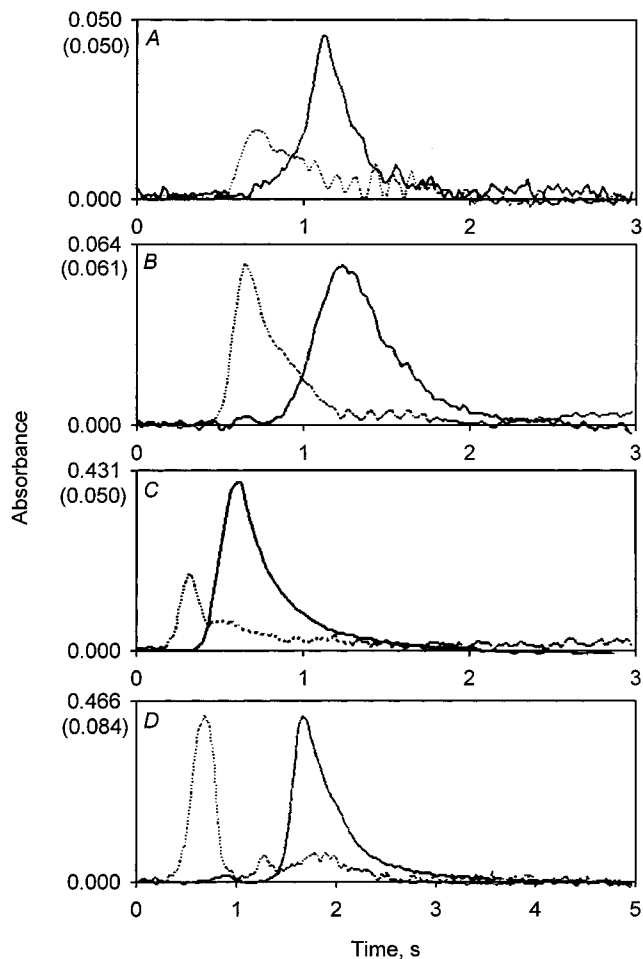
**Figure 2.** Influence of the hydrogen peroxide concentration on the relative standard deviation values. Concentrations of the baby food samples were 1.5% w/v for manganese, 10% w/v for nickel, 20% w/v for cobalt, and 7% w/v for copper. Suspensions contained 0.1% w/v Triton X-100 and 1% v/v nitric acid.



**Figure 3.** Extraction of the metals into the liquid phase from baby food suspensions by addition of nitric acid. Samples were 1.5% w/v mixed fruits slurry for manganese, 7% w/v hake slurry for copper, and 20% w/v vegetables slurry for nickel and cobalt.

(RSD) improved. This beneficial effect was especially important for cobalt and nickel because the high suspension concentrations used for these metals produced a build-up of carbonaceous residues inside the tube. Figure 2 shows the results obtained. Thus, 30% v/v concentrated hydrogen peroxide was added to the suspensions.

The addition of nitric acid to the suspension was deemed necessary to obtain good sensitivity and to increase reproducibility because the solubilizing action of the acidic suspending medium results in a fraction of the analyte being extracted into the supernatant. An increase in the degree of extraction increases reproducibility because sampling problems are minimized. Figure 3 shows the results obtained when the percentage of the acid was varied between 0.2 and 3% v/v. Suspensions from different baby food samples were prepared as described in the Experimental Procedures and centrifuged. The analyte contents were then determined in the supernatant. As expected, the presence of nitric acid in the suspension media considerably increased the



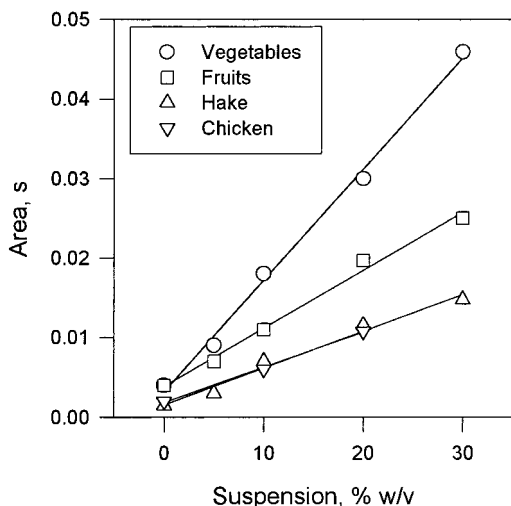
**Figure 4.** Atomization profiles for manganese, copper, cobalt, and nickel from baby food suspensions. The broken lines show the background signals.

extraction efficiency of the analytes into the liquid phase. Similar results were obtained for several different baby food samples. A 1% concentration value was selected because this led to almost 100% recoveries of the analytes in the supernatant and the pyrolytic material of the graphite atomizer tube was not destroyed.

Figure 4 shows the atomization profiles (solid lines) for manganese, copper, cobalt, and nickel obtained under the optimized experimental conditions. These profiles were similar to those found for aqueous standards. The background signals (broken lines) were not very high.

**Influence of the Suspension Concentration and Study of Matrix Effect.** The influence of the suspension concentration on the analytical signal for nickel when using different types of baby foods is shown in Figure 5. The response increased linearly with increasing concentrations up to a 30% w/v concentration. Higher proportions of sample in the suspension are not recommended because of the difficulty of obtaining reproducible sampling. Similar results were obtained for the other metals; however, the linearity range varied according to the analyte and its level in the sample. The slopes of aqueous calibration and standard additions calibration graphs were compared to establish possible interferences due to the matrix. Table 3 shows the results obtained. Each graph was constructed from four points and each point represents the mean of three replicate observations. As can be seen, the slopes obtained for





**Figure 5.** Influence of the suspension concentration for atomization of nickel from different baby food samples.

aqueous standards and standard additions to different baby food suspensions were quite similar. The slopes of the best-fit regression lines for standard additions to the different suspensions varied by 7.5% (RSD) for copper, 2.0% for manganese, 6.3% for cobalt, and 6.6% for nickel. Consequently, direct calibration against aqueous standard solutions could be carried out for suspensions with concentrations of samples not exceeding 30% w/v.

**Calibration, Results, and Statistical Study.** Table 1 shows the characteristics of the calibration graphs for copper, cobalt, nickel, and manganese. The detection limits were calculated for 10 successive injections of the blank and using the  $3\sigma$  criterium for the maximum recommended suspension concentration (20% w/v).

Different baby food samples were analyzed by using the proposed procedure as well as a procedure based on a mineralization step using a closed system. Table 4 summarizes the results obtained. The paired  $t$ -test revealed no significant difference between the results obtained using either procedure (level of significance 0.05,  $p = 0.243$  for copper,  $p = 0.856$  for manganese,  $p = 0.180$  for nickel, and  $p = 0.317$  for cobalt). Cobalt and nickel were found at low concentrations, while copper and manganese appeared at higher concentrations. A three way ANOVA test was then used to prove the existence of a statistically significant difference between the groups, with the metal, the type of baby food, and the method used for the analysis being considered as the three factors. The Tukey test was selected to carry out all the pairwise multiple comparison procedures. The difference in the mean values among the different levels of factor A (metal) shows that there is a statistically significant difference ( $F = 9255$ ,  $p < 0.001$ ) and each group differs from the others. For factor B (type of baby food) a similar conclusion is obtained, each group differing from the others ( $F = 1224$ ,  $p < 0.001$ ). Finally, the difference in the mean values of factor C (method of analysis) is just due to random sampling variability and there was no statistically significant difference ( $F = 0.730$ ,  $p = 0.415$ ), confirming the results obtained from the paired  $t$ -test.

The reliability of the method was further corroborated by using several certified reference materials (Table 5). Application of both the paired  $t$ -test and the Wilcoxon signed rank test concluded that there was good agree-

ment (level of significance 0.05) between the certified values and the results obtained ( $p = 0.150$  for copper,  $p = 0.074$  for manganese,  $p = 0.875$  for nickel, and  $p = 0.130$  for cobalt). The three-way ANOVA test was also applied taking the metal, the type of certified reference material, and the method employed for the analysis as the three factors. Again, the results showed that using the different levels of factor A (metal) there was a statistically significant difference ( $F = 299.6$ ,  $p < 0.001$ ) and each group differed from the others. For factor B (type of certified reference material), each group also differed from the others ( $F = 301.4$ ,  $p < 0.001$ ). For factor C (results obtained by using the proposed method or certified), the difference is again due to random sampling variability and there was no statistically significant difference ( $F = 0.159$ ,  $p = 0.415$ ).

**Conclusion.** Different types of baby food samples were analyzed to determine the contents of different oligoelements. Cobalt and nickel were found at low concentrations, while copper and manganese appeared at higher concentrations. A previous mineralization step is not necessary because suspensions prepared from the samples are directly injected into the atomizer as slurries. The addition of both hydrogen peroxide and nitric acid to the samples considerably reduces the deposition of carbonaceous residues, which improves reproducibility. The procedures are rapid and accurate and can be applied to routine multielemental analysis in the nutritional and toxicological quality control of baby food samples.

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**Table 3. Slopes of Standard Addition Calibration Graphs for Different Baby Food Samples**

sample	slope <sup>a</sup> , s mL ng <sup>-1</sup>			
	copper (7% w/v)	cobalt (20% w/v)	nickel (20% w/v)	manganese (2% w/v)
aqueous standards	0.0140 ± 0.0003	0.003 96 ± 0.000 11	0.002 34 ± 0.000 11	0.0301 ± 0.0010
chicken with rice	0.0150 ± 0.0036	0.003 40 ± 0.000 33	0.002 31 ± 0.000 21	0.0312 ± 0.0012
hake with rice	0.0125 ± 0.0022	0.003 53 ± 0.000 28	0.002 02 ± 0.000 07	0.0310 ± 0.0025
mixed vegetables	0.0149 ± 0.0021	0.003 51 ± 0.000 15	0.002 19 ± 0.000 31	0.0306 ± 0.0032
mixed fruits	0.0150 ± 0.0058	0.003 43 ± 0.000 27	0.002 06 ± 0.000 18	0.0297 ± 0.0037

<sup>a</sup> Mean ± standard deviation (*n* = 3).**Table 4. Metal Contents in Different Baby Food Samples**

sample	metal content <sup>a</sup>							
	copper, µg/g		manganese, µg/g		nickel, ng/g		cobalt, ng/g	
	suspension	mineralization	suspension	mineralization	suspension	mineralization	suspension	mineralization
chicken with rice	0.356 ± 0.04	0.358 ± 0.03	0.816 ± 0.006	0.805 ± 0.01	10.5 ± 1	10.3 ± 2	not detected	0.85 ± 0.12
hake with rice	0.471 ± 0.02	0.476 ± 0.01	0.464 ± 0.004	0.487 ± 0.006	10.1 ± 1	11.5 ± 1	2.27 ± 0.14	2.44 ± 0.10
mixed vegetables	0.820 ± 0.03	0.782 ± 0.02	1.44 ± 0.024	1.46 ± 0.023	85.1 ± 2	92.0 ± 1	12.6 ± 1.1	16.6 ± 0.5
mixed fruits	0.808 ± 0.04	0.755 ± 0.01	0.680 ± 0.005	0.657 ± 0.01	33.2 ± 2	35.7 ± 1	2.70 ± 0.26	3.11 ± 0.24

<sup>a</sup> Mean ± standard deviation (*n* = 3).**Table 5. Results for the Certified Reference Materials**

sample	metal content <sup>a</sup>							
	copper, µg/g		manganese, µg/g		nickel, µg/g		cobalt, µg/g	
	suspension <sup>a</sup>	certified	suspension <sup>a</sup>	certified	suspension <sup>a</sup>	certified	suspension <sup>a</sup>	certified
total diet (HDP)	3.3 ± 0.2	3.18 ± 0.19	12.4 ± 0.2	12.9 ± 0.58	301 ± 21	271 ± 38	not determined	not certified
oyster tissue (SRM 1566a)	61.6 ± 2.0	66.3 ± 4.3	11.0 ± 0.3	12.3 ± 1.5	1.96 ± 0.1	2.25 ± 0.44	0.50 ± 0.07	0.57 ± 0.11
bovine liver (SRM 1577b)	154 ± 1	160 ± 8	11.3 ± 0.3	10.5 ± 1.7	not determined	not certified	0.21 ± 0.02	(0.25)
rice flour (SRM 1568a)	2.3 ± 0.1	2.4 ± 0.3	18.3 ± 0.2	20.0 ± 1.6	not determined	not certified	not detected	(0.018)
citrus leaves (SRM 1572)	16.1 ± 0.4	16.5 ± 1.0	20.5 ± 0.8	23 ± 2	0.58 ± 0.1	0.6 ± 0.3	not detected	(0.02)
apple leaves (SRM 1515)	5.4 ± 0.2	5.64 ± 0.24	53 ± 1.2	54 ± 3	0.84 ± 0.01	0.91 ± 0.12	0.077 ± 0.008	(0.09)

<sup>a</sup> Mean ± standard deviation (*n* = 4).

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