

Lead and Cadmium in Baby Foods

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A solvent-extraction/atomic-absorption method for the determination of lead and cadmium has been applied to a range of baby foods. Results for all samples examined were well below the U.K. limit for lead in such foods.

In 1972, the Working Party on the Monitoring of Foodstuffs for Heavy Metals reported¹ the lead content of canned baby foods to have a mean value of 0.24 p.p.m., with a range of 0.01–1.1 p.p.m. In the Bristol laboratory, similar lead levels had been found in six samples of canned savoury baby foods which ranged from 0.25 to 0.65 p.p.m. of lead, and had a mean value of 0.38 p.p.m. Subsequently, the Statutory Limit for lead in baby foods* was reduced to 0.5 p.p.m.

This paper considers the analytical method used and the results obtained for a variety of baby foods submitted for examination since the introduction of the amended legislation. These samples have been examined for

- (a) Lead, in order to confirm that measures taken by the manufacturers had lowered the level of lead sufficiently in all baby foods to comply with the new Regulations.
- (b) Cadmium, because of the increasing concern about ingestion of this element, which has been suggested to provide 'the most insidious and most widespread health hazard of any of the trace elements'². On excessive accumulation of cadmium in the kidneys (greater than 200 p.p.m., wet weight) renal damage is likely to occur, evidenced by mild proteinuria³. Acute poisoning produces tubular proteinuria accompanied by osteomalacia and painful pseudo bone fractures³, thus accounting for the Japanese description as '*itai-itai*' (literally 'ouch-ouch') disease. However, in spite of cadmium's extreme toxicity, a recent report⁴ maintains that there is no cause for alarm nor reason to set Statutory Limits, since, in the U.K., "cadmium occurs at very low levels in the general food supply".

In order to achieve low-level analysis of lead and cadmium in a reasonable time using the laboratory's existing instrumentation, flame atomic absorption preceded by a solvent-extraction/concentration step was employed. A slightly more involved extraction method was employed by Thomas, Roughan and Watters⁵ for the analysis of lead and cadmium in vegetables. Baetz and Kenner⁶ used a chelating ion-exchange resin to separate and concentrate seven heavy metals prior to conventional atomic-absorption analysis. Whilst their method has the advantage of determining several metals in one sample digest, the sensi-

* The Lead in Food (Amendment) Regulations, 1972 (S.I. 1972, No. 1843); came into operation on 1st January, 1973.

vities and detection limits for lead and cadmium are inadequate for the present purpose. Other methods which appear to be suitable are polarography⁷⁻¹⁰ and anodic stripping voltammetry¹¹⁻¹⁵. The use of colorimetric methods¹⁶⁻²⁰, which are generally satisfactory for lead and cadmium determinations, would have been time consuming if used for the determination of both metals on the number of samples involved. Rapid and sensitive flameless atomic-absorption methods²¹⁻²³ have been reported for both lead and cadmium, but they generally require the use of sophisticated and quite expensive instruments.

Apparatus

Before use, all items of glassware and silica dishes should be immersed in 5 per cent. v/v hydrochloric acid (reagent grade) for several hours, and then rinsed with double-distilled water.

1. Silica dishes with lips, volume approx. 30 ml.
2. Graduated 5-ml and 1-ml pipettes.
3. 25-ml Volumetric flasks with plastic stoppers.
4. Atomic absorption spectrophotometer (e.g. Hilger and Watts Atom-spek H1170). The operating conditions for lead and cadmium, using an Atom-spek H1170, are shown below.

	Lead	Cadmium
Lamp current (mA)	6	5
Wavelength (nm)	217.0	228.9
Slit width (μ m)	100	45
Burner height (mm)	9	9
Acetylene (litre min ⁻¹ at 5 psig)	0.75	0.75
Air (litres min ⁻¹ at 30 psig) ..	2	2
Pen response time (sec.) ..	3.5	3.5
Scale expansion	1.0	0

5. Recorder (e.g. Servoscribe Flat-bed.)

Reagents

1. *Water*: Double-distilled, using silica-sheathed elements.
2. *Nitric acid* (S.G. 1.42): Low-in-lead quality.
3. *Hydrochloric acid* (S.G. 1.17): Low-in-lead quality.
4. *Diethylammonium diethyldithiocarbamate (DDDC)*: A 1 per cent. w/v solution in methyl isobutyl ketone (MIBK). The solution may be kept for several weeks without deterioration.
5. *Methyl isobutyl ketone solvent*: A saturated solution of water in MIBK.
6. *Ascorbic acid*: A freshly prepared, 10 per cent. w/v aqueous solution.
7. *Standard solution of lead and cadmium*: A 2 per cent. w/v solution of hydrochloric acid containing 10 p.p.m. of lead and 2 p.p.m. of cadmium.

Method

Dry ash (see Note 1.) 10 g of the homogenised sample (weighed to nearest 0.1 g) at 450–500°C in a silica dish until the ash is grey or white. Moisten with diluted nitric acid/water (1 + 9) and briefly re-ash if necessary. Treat the ash with 5 ml of water followed by 5 ml of hydrochloric acid, and evaporate to dryness on a steambath. Add 1.0 ml of hydrochloric acid and 3–5 ml of water, stirring with a glass rod, filter through a small No. 4 paper into a 25-ml volumetric flask, and make up to the mark with dish and rod rinsings. Prepare aqueous standards in 25-ml calibrated flasks using 0, 0.10, 0.20, 0.50 and 1.00 ml of the standard lead/cadmium solution. To each flask add 1.0 ml of hydrochloric acid and make up to the mark with water (see Note 2.).

To the blank, standards and samples add 0.5 ml of ascorbic acid solution and invert to mix the contents. Then, without delay, add 1.50 ml of DDDC solution, stopper, and shake the flasks for 30 seconds. When the phases have separated, tap the flasks on the bench to remove solvent globules caught on the sides of the flasks, and aspirate the organic layers into the spectrophotometer first for cadmium and then for lead. Spray MIBK solvent before and after each sample or standard in order to establish the baseline. Construct calibration graphs of the responses to the aqueous standards and hence determine the cadmium and lead contents in each sample.

Note 1. Char milk powders, cereals and dehydrated foods over a Bunsen burner before ashing. A dish larger than the 30-ml size is preferable for these materials.

Note 2. The samples and standards may be left at this stage for several days, but once the extraction process has been started, the analysis should be completed as soon as possible.

Discussion

Dry ashing is preferred to wet oxidation for the types of samples under examination, since little attention is required during ashing and subsequent pH adjustment is straightforward, in addition to other advantages cited by several authors^{8,24–26}. Dry ashing has been reported to cause metal loss by volatilisation, by adsorption on unburned carbon or by formation of insoluble silicates²⁷. Nevertheless, no evidence of significant lead or cadmium loss has been found in this study using ashing temperatures of 450–500°C, followed by hydrochloric acid treatment at 100°C to break down any insoluble silicates. Similar findings have been published for lead, cadmium, zinc and copper, with respect to particulate air pollutants on filter papers²⁸.

It is convenient to dissolve the ash in a measured volume of hydrochloric acid in order to achieve the correct pH for solvent extraction. The resulting solution (1 ml of concentrated acid to 25 ml) is 0.5 N in hydrochloric acid, at which acid strength all phosphates should be dissolved.

Of the elements likely to be present in the food digests, only iron, copper and zinc could interfere in the proposed determinations. These elements are usually masked by forming their cyanide complexes at pH 8.5²⁹. In the preceding method, however, it has been found necessary to eliminate completely the interference from iron only by reducing any Fe^{III} to Fe^{II} (using ascorbic acid) prior to the extraction step³⁰. Three series of calibrations for 0–1 μg of cadmium and 0–5 μg of lead were carried out using this approach:

- (a) standard calibrations
- (b) calibrations in the presence of 50 μg each of iron^{III}, copper and zinc.
- (c) calibrations in the presence of 100 μg each of iron^{III}, copper and zinc.

The results are shown in Figure I. Evidently, lead is subject to slightly more interference than cadmium though the effect causes no more than a 15 per cent. decrease in response even in calibration (c). Moreover, since such excessive amounts of iron, copper and zinc as used in (c) are unlikely to be present in 10 grammes of baby food, any interference by these metals should be within experimental error.

Experiments indicated that the lead-DDDC complex was stable for several hours, whilst that of cadmium was subject to slight decomposition (judged by a decrease of 10 to 20 per cent. in the instrument response). For this reason cadmium was always determined first, and the lead determination was completed within three hours of extraction as recommended by Brooks, Presley and Kaplan³¹. Nix and Goodwin³² showed that the sodium diethyldithiocarbamate complexes of copper, iron, cobalt, nickel, chromium, lead, zinc, but not of manganese, were stable for at least 400 minutes.

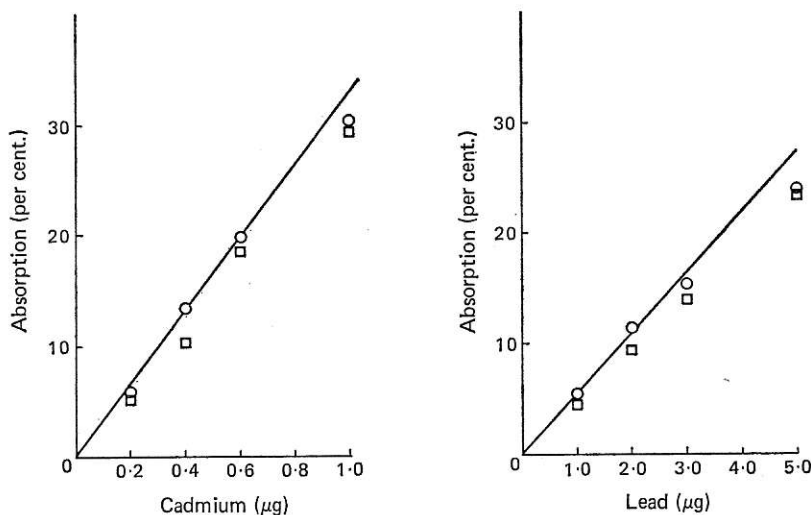


FIG. 1. Calibration curves and the effects on them of iron, copper and zinc ions.

The lines show the standard calibration curves.

○ Calibrations in the presence of 50 μg each of Fe, Cu, and Zn.

□ Calibrations in the presence of 100 μg each of Fe, Cu, and Zn.

TABLE I

TYPICAL RECOVERIES OF LEAD (0.5 P.P.M.) AND CADMIUM (0.1 P.P.M.) ADDED TO BABY FOOD

Food	Levels before addition		Recovery of	
	Cadmium <i>parts per million</i>	Lead <i>parts per million</i>	Cadmium <i>per cent.</i>	Lead
Ostermilk Two	0.017	0.07	90	90
Babymilk 2	0.006	0.07	90	95
Chocolate cereal	0.052	0.50	90	70

TABLE II

REPRODUCIBILITY OF THE METHOD: REPLICATE ANALYSES ON A SAMPLE OF DRIED MILK

Lead <i>parts per million</i>	Cadmium <i>parts per million</i>
0.080	0.0090
0.065	0.0090
0.075	0.0055
0.065	0.0080

Recovery experiments were performed on powdered milk and cereal products, which were assumed to be homogeneous when packaged. The results of several standard addition experiments are shown in Table I.

The results of four replicate analyses on a sample of dried milk (see Table II) indicate that the method is adequately reproducible, bearing in mind the small quantities of lead and cadmium involved.

For the ranges 0–10 μg of lead and 0–2 μg of cadmium linear (or sometimes slightly curved) calibrations were obtained. Details of sensitivities, noise levels etc., are shown in Table III. Thus, for a 10-g sample the detection limits were 0.002 p.p.m. of cadmium and 0.02 p.p.m. of lead. Smaller samples (2–4 g) were wet-oxidised using the Thompson-Blanchflower apparatus³³ in an attempt to shorten the time of analysis. However, the small time-saving was offset by problems of relatively high reagent blanks and poor recoveries of added lead and cadmium.

TABLE III

INSTRUMENTATION: BLANK VALUES, SENSITIVITIES, NOISE LEVELS AND DETECTION LIMITS

Parameter	Lead	Cadmium
Typical blank* value (per cent. absorption)	2.0	1.5
Sensitivity ($\mu\text{g}/1$ per cent. absorption)	0.18	0.03
Maximum noise level (per cent. absorption)	0.5	0.3
Detection limit ($2 \times$ noise level; μg)	0.2	0.02

- * Note 1. Replicate determinations were in excellent agreement.
 2. Virtually identical values were obtained for blanks that were carried through the ashing, hydrochloric acid treatment and filtration stages.

Results

Results are set out in Table IV. Lead is reported to the nearest 0.05 p.p.m. and cadmium to the nearest 0.005 p.p.m. unless the food required reconstitution (and consequent dilution) before consumption.

TABLE IV

THE LEAD AND CADMIUM CONTENTS OF VARIOUS BABY FOODS

	Sample in the reconsti- tuted food	Metal levels in the reconstituted food	
	<i>per cent.</i>	Lead <i>parts per million</i>	Cadmium <i>parts per million</i>
<i>(a) Dried foods, rusks (all in packets)</i>			
Milk food	13	<0.01	0.003
Milk food (2 samples)	13	<0.01	0.003
Milk food	14	<0.01	0.001
Milk food (4 samples)	14	<0.01	0.001-0.004
Triple Pack;			
Groats	6	<0.01	0.002
Mixed cereal	15	0.03	0.005
Baby rice	8	0.01	0.004
Baby cereal (groats)	6	<0.01	0.003
Baby rice	8	0.01	0.002
High protein baby food; 4 samples	24	0.05-0.12	0.004-0.006
Orange, egg and honey pudding	12	0.02	0.003
Vegetable and lamb (2 samples)	10	0.01	0.003
		0.04	0.002
Baby cereal	10	0.02	0.008
Twin pack;			
Baby rice cereal with egg	13	0.08	0.007
Baby rice cereal chocolate flavour	19	0.10	0.010
Strawberry cereal	23	0.07	0.010
Bone and vegetable food	17	<0.01	0.010
Beef dinner	10	0.02	0.004
Vegetables and liver	10	0.02	0.005
Orange cereal	25	0.09	0.006
Swiss baby food	36	0.07	0.009
Rusk fingers	100	0.10	0.055
Baby rusks	100	0.05	0.065
Teething rusks	100	0.15	0.025
<i>(b) Canned foods</i>			
Chicken casserole with vegetables		0.05	0.010
Egg custard with rice		0.10	0.030
Vegetables with beef		0.05	0.040
Apple dessert		0.15	0.020
Apricot and rice		0.05	0.080
Chocolate pudding		0.10	0.030
Beef dinner		0.20	0.030
<i>(c) Bottled foods</i>			
Vegetables with chicken		0.10	0.055
Egg custard and rice		0.10	0.025
Apples		0.05	0.025
Gripe water		<0.05	<0.005
Honey for baby		0.15	0.060
Roast chicken and vegetables with bacon		0.10	0.010
Roast turkey and vegetables with bacon		0.10	0.010

Discussion

All values for lead are well below the legal limit of 0.5 p.p.m., the highest value found being 0.2 p.p.m. In Table V the mean lead and cadmium contents of four types of non-reconstituted baby foods are shown.

TABLE V
MEAN LEAD AND CADMIUM CONTENTS OF SOME TYPES OF BABY FOODS

Food	Number of samples	Mean		Other Authors ^{1,4} mean values	
		Lead	Cadmium	Lead	Cadmium
		<i>parts per million</i>		<i>parts per million</i>	
Dried Milk	8	0.05	0.020	0.08	<0.01
Dried Cereal	15	0.27	0.035	0.11	<0.02
Canned Foods	7	0.10	0.036	0.24	<0.01
Bottled Foods	7	0.09	0.026	0.05	<0.01

It is significant that the mean lead level for the canned baby foods is virtually the same as that for the bottled foods. Normally, the lead levels in canned foods are enhanced as a result of contamination during the canning process, or through release of lead from the can, mainly from its soldered seam. For example, a recent survey³⁴ of fruit and vegetables (not baby foods) indicated a mean lead value of 0.08 p.p.m. for fresh produce and a value of 0.56 p.p.m. for canned varieties. In addition, Table V shows that the mean lead level for canned baby foods (admittedly from a small number of samples) is lower than that found previously, both in this laboratory (see introduction) and elsewhere¹. This improvement could possibly be attributed in part to the recent use of specially purified tin and of low-lead solder by the can manufacturers. Cereal foods showed an unexpected increase in lead content over the previous value. Nevertheless, the general picture with respect to lead content appears to be satisfactory.

The mean cadmium values are all greater (by factors of 2 to 4) than those for baby foods given in a recent report⁴ which also gives similarly low total diet mean cadmium contents (0.01–0.02 p.p.m.). However, the present results do fall into line with those of other studies:

- (i) In a total diet study of children's food in the U.S.A.³⁵ a range of 0.027 to 0.062 p.p.m. of cadmium was found.
- (ii) Another U.S.A. survey³⁶ of 360 total diet samples showed 244 residues of cadmium in the range 0.01–0.38 p.p.m.
- (iii) A Rumanian survey¹⁷ of 14 animal foods and 16 plant foods indicated that a daily ration of food contained an average of 0.038–0.063 p.p.m. of cadmium.

As a result of the latter survey, a general tolerance limit of 0.05 p.p.m. of cadmium was proposed, with the exception of beef, fish, preserves and tomato pulp where 0.10 p.p.m. was suggested. Of the baby foods studied, only a few

would exceed this proposed lower limit for cadmium, and not to any great extent.

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