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PII: S0308-8146(96)00328-7

Food Chemistry, Vol. 60, No. 1, pp. 123–128, 1997

0308-8146/97 $17.00 + 0.00
Analytical, Nutritional and Clinical Methods Section

Determination of manganese and chromium in foods by atomic absorption spectrometry after wet digestion

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(Received 5 March 1996; revised version received 10 October 1996; accepted 10 October 1996)

Wet digestion procedures using acid mixtures of $HNO_3/H_2SO_4/HClO_4$ and HNO_3/H_2SO_4 were investigated for their effectiveness for decomposition of food samples prior to determination of manganese (Mn) and chromium (Cr) by flame and Zeeman graphite furnace atomic absorption spectrophotometry. The addition of hydrofluoric acid (HF) to the mixture of HNO_3/H_2SO_4 was also investigated for determination of Cr. All the acid mixtures tested were found to be satisfactory, but, for reasons of safety, HNO_3/H_2SO_4 was the method of choice. No apparent matrix interferences or losses of analytes were encountered with the method used. Analysis of selected food samples found relatively high levels of Mn and Cr in most cereal products. Meats, dairy products (except for Cr in cheese), vegetables and fruits contained relatively low levels of both elements. © 1997 Elsevier Science Ltd

INTRODUCTION

Manganese (Mn) and chromium (Cr) are recognised as essential trace elements for humans, and several of their metabolic roles have been determined. These include Mn-containing enzyme systems (Hurley, 1984) and Cr involvement in insulin function (Offenbacher & Pi-Sunyer, 1988). However, for neither of the elements have human requirements or levels of absorption from the diet been clearly determined. These questions will remain unanswered until accurate and reliable data on concentrations of the elements in foods are available. Unfortunately, up to the present time, technical problems with analytical techniques have limited the amount of this data available.

Determination of Mn and Cr is a challenge to nutritional analysts because of their normally low levels in many foods. Contamination from sample preparation has been a persistent problem in the past, particularly for Cr analysis (Veillon, 1986). Prior to instrumental analysis, samples were decomposed by means of wet digestion or dry ashing techniques. Atomic absorption spectrometry (AAS) utilising both flame (F) and graphite furnace (GF) is the most widely used analytical technique for both elements in a wide range of foods and other biological samples (Jones *et al.*, 1975; Cary & Rutzke, 1983). Problems of spectral interferences such as non-specific background absorption caused by high concentrations of halides and inorganic acids in the sample matrix still can occur, especially with GF-AAS. Chlorides, for example, can suppress the analytical signal for Mn (Hulanicki *et al.*, 1990). Background correction of non-atomic absorption, especially in Cr analysis and the use of a high-intensity tungsten-iodide lamp may be required or, better still, Zeeman effect background correction (Barnett *et al.*, 1985; Carnick *et al.*, 1986).

The aim of the study was to contribute to the establishment of more reliable, routine methods for the determination of Mn and Cr in foods by investigating the efficiency of various wet digestion procedures and the use of Zeeman effect as background correction in GF-AAS. The study would also provide further information on levels of Mn and Cr in foods and to contribute to the food composition data base in Australia which is currently lacking.

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Table 1. Operating parameters for Mn for F-AAS

Wavelength	279.5 nm
Band width	0.2 nm
Lamp current	5 mA
Flame	Air/acetylene
Scale expansion	×5

MATERIALS AND METHODS

Apparatus

A flame atomic absorption spectrophotometer (Model AA6, Varian Techtron) coupled to a Rikadenki strip-sheet chart recorder, and an Hitachi Model Z-7000 Zeeman graphite furnace atomic absorption spectrophotometer with autosampler coupled to a micropressor with visual display unit and a printer, were used.

Reagents and preparation

All preparation of standards and samples carried out under clean room conditions using deionised water, specific resistivity of 15–18 MΩ cm (Elgastat Spectrum Water Purification Unit) and analytical grade (Aristar, BDH) nitric (HNO_3), sulphuric (H_2SO_4), perchloric ($HClO_4$), hydrochloric (HCl) and hydrofluoric (HF) acids. Mn stock standard (1000 mg litre^{-1}) was prepared by dissolving 1.5825 g of MnO_2 (Specpure, UK) in HCl, and Cr stock standard (1000 mg litre^{-1}) was prepared by dissolving 2.8349 g of $K_2Cr_2O_7$ (Univar, Ajax) in HNO_3.

Standard reference materials (National Institute of Standards and Technology, Gaithersburg, USA), of Non-fat Milk Powder 1549, Tomato Leaves 1573, Bovine Liver 1577a and Brewer's Yeast 1569 were used for validation of the method.

Working standard solutions

All working standards were prepared in 4% (v/v) H_2SO_4 to match the acid concentration in digestion solutions. Combined working standards for Mn and Cr were 1.0, 2.0, 4.0, 6.0 and 8.0 μg litre^{-1} using the Zeeman GF-AAS. For Mn analysis using the F-AAS, concentrations were 100, 200, 300 and 400 μg litre^{-1} were used.

Cleaning of apparatus

All glassware and plastic ware were soaked in Dextran detergent solution (3%) for 24 h, thoroughly rinsed in deionised water, soaked in diluted HCl (2%, v/v) for at least 24 h and, when required, were rinsed thoroughly with deionised water before use.

Collection of samples

Foods collected was not intended to cover the full range of the general Australian diet. They were not randomly sampled, but were mainly collected as duplicate samples of items consumed by children in Brisbane households during a study of trace element intakes. Details of this study have been reported elsewhere (Reilly *et al.*, 1990). Some additional foods not easily obtained from the homes were purchased in Brisbane local stores. All samples were frozen and kept at −20°C until required for analysis.

Sample digestion

Five to 15 g of moist or wet foods, and 1–2 g of dry foods were sampled. Samples were accurately weighed and transferred to 150 ml conical flasks. A mixture of HNO_3–H_2SO_4 (12:2 ml) or HNO_3–H_2SO_4–$HClO_4$ (12:2:2 ml) was added. The samples were left at room

Table 2. The operating conditions and instrumental parameters for Zeeman GF-AAS

	Chromium		Manganese	
	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
Operating conditions				
Dry	80–120	20	80–120	30
Dry	120–250	15	120–250	20
Ash	700–1000	20	500–800	25
Ash	1000–1200	8	800–1200	5
Atom	2600–2600	5	2500–2500	5
Clean	2800–2800	3	2800–2800	3
Instrumental parameters				
Cuvette	Pyrolytic		Pyrolytic	
Carrier gas	Argon (200 ml min^{-1})		Argon (200 ml min^{-1})	
Interrupt gas	Off		Off	
Sample volume	20 μl		20 μl	
Measurement mode	Peak height		Peak height	
Lamp	Hallow cathode		Hallow cathode	
Wavelength	359.3 nm		279.6 nm	
Lamp current	7.5 mA		7.5 mA	
Slit width	1.3 nm		0.4 nm	

temperature overnight. This avoided the vigorous fuming of nitrogen dioxide during heating. The following morning the glass funnels were inserted into the flasks for refluxing, and gradually heated on the hot plate. The presence of H_2SO_4 prevented the solution from drying out at increased temperature. However, H_2SO_4 could cause charring and if this occurred, as in the case of foods with a high carbohydrate or fat content, HNO_3 was added dropwise and refluxing continued. The digestion was completed with the appearance of white fumes of sulphur trioxide or perchloric acid. The entire procedure was also carried out for two blanks, containing the same amount of acids as the samples. Digested solutions were then transferred into graduated test tubes and made up to 20 ml with deionised water.

For the analysis of Cr with HF added to the acid mixture, the digestion was carried out in a platinum crucible which was heated on the hot plate until fumes of sulphuric acid appeared and a silica-free solution was obtained. The sample was diluted in a polypropylene container.

F-AAS method

Mn levels in foods were determined using F-AAS and the signal peak height was recorded. Instrument optimisation was set according to the manufacturer's instruction manual and the operating conditions are listed in Table 1. Initially, a sequential deuterium lamp was used for background correction, and, since no background interference was observed, use of the deuterium lamp was discontinued. Prior to analysis, the nebuliser was cleaned by aspirating 20 ml of deionised water. The blank and standards were aspirated first, followed by the unknown samples. Deionised water was aspirated between each sample after duplicate readings were taken. The unknown sample concentrations were determined from the calibration graph.

Zeeman GF-AAS method

Aqueous standards were used to determine appropriate ashing and atomisation temperatures for Mn and Cr and to obtain an optimum sensitivity without loss of elements. Table 2 lists the operating conditions used for the method. Samples were thoroughly mixed by inversion before being transferred into the autosampler cups in a sequence of blank and standards of ascending concentrations. The results were automatically calculated by the coupled microprocessor.

RESULTS AND DISCUSSION

Digestion and analytical procedures

Although initial results indicated that NHO_3–H_2SO_4 or HNO_3–H_2SO_4–$HClO_4$ mixtures were equally effective for digesting food samples for Mn analysis, the $HClO_4$-free mixture was subsequently used for all analyses for reasons of safety. The presence of perchloric acid during digestion of food can result in the formation of metal perchlorates which are explosive in nature and when possible their formation should be avoided (Analytical Methods Committee, 1960).

F-AAS has been a widely accepted method for analysis of Mn in a variety of biological materials (Evans *et al.*, 1980). In this study, F-AAS was found to be rapid with good accuracy for Mn determination in most foods. No background absorption or matrix interference was observed and the use of sequential deuterium lamp background correction was not required. However, for foods with low levels of Mn, the more sensitive Zeeman GF-AAS was required. Again, no matrix interference was encountered during the analysis.

Reports on the use of $HClO_4$ with the NHO_3–H_2SO_4 mixture for digestion of food samples for Cr analysis have been confusing and contradictory. Results produced were particularly poor and varied widely. This could be due in part to loss of volatile Cr as chromyl chloride formed in the presence of $HClO_4$ (Gorsuch, 1962; Agemian & Chau, 1976). In this study, the presence of $HClO_4$ was found to cause a memory effect on the pyrolytic cuvette and resulted in poor reproducibility after 15–20 firings. Several cleaning attempts (by 'boosting' the temperature to 3000°C) after the atomisation stage did not remove the memory effect. It appears that the presence of $HClO_4$ attacks the graphite of the cuvette and thus enhanced the memory effect by causing some retention of Cr as a carbide (Matousek & Powell, 1986). It was also found that $HClO_4$ drastically shortened the life of the pyrolytic cuvette.

Digestion of samples using a HNO_3–H_2SO_4 mixture gave good reproducibility except when the sample contained a high level of carbohydrate or fat which often left incompletely decomposed material floating in the solution. The digestion was improved in such cases by reducing the size of the sample (1–2 g for wet foods) and by increasing the digestion time and the amount of HNO_3. This digestion mixture gave good recoveries

Table 3. The recovery of Mn from standard reference materials after HNO_3–H_2SO_4 digestion

Material	n^a	This study (mean ± SD)	Certified value	Recovery
Non-fat Milk 1549	10	0.28 ± 0.03^b	0.26 ± 0.06	108
Tomato Leaves 1573	5	225 ± 6^c	238 ± 7	95
Bovine Liver 1577a	6	9.7 ± 0.3^c	9.9 ± 0.8	98

All concentrations are expressed in $\mu g\ g^{-1}$.
[a] n, number of samples analysed.
[b] Results were obtained by Zeeman GF-AAS analysis.
[c] Results were obtained by F-AAS analysis.

with no apparent losses of MN (Table 3) and Cr (Table 4) from standard reference materials.

As shown in Table 4, Brewer's Yeast standard reference material was used for validation of the method after digestion with the HNO_3–H_2SO_4 mixture. Recoveries were very poor, apparently due to the presence of silica in the yeast. Similar findings have been reported by other investigators who found that addition of HF is necessary to remove the siliceous residue in the form of silicate tetrafluoride (SiF_4) (Cary, 1985; Chao & Pickett, 1980; Cary & Rutzke, 1983). When HF was added to the NHO_3–H_2SO_4 mixture, recovery of Cr in the Brewer's Yeast reference material was very good and well within the range of certified values (Table 4). The digestion procedure with the addition of HF was further investigated in this study for the analysis of Cr in a variety of food samples.

Certain other foods (e.g. lettuce) have been reported to contain appreciable amounts of silica which could interfere with Cr recovery (Arafat & Glooschenko, 1981). These food samples were digested with the HF-containing acid mixture and results were compared with samples digested without HF. No significant differences were found between these two treatments (Table 4). This finding indicates that the presence of silica in these foods appeared to have minimal effects on the analysis of Cr. This view was further supported by the finding that there was no significant difference in recovery of Cr when Tomato Leaves standard reference material was digested with and without HF (Table 4). It is shown in this study that addition of HF in acid mixture was unnecessary for the analysis of Cr.

Accuracy and detection limit

The accuracy of the methods was assessed by analysing several appropriate standard reference materials. It can be seen in Table 3 that the recoveries for Mn were within range of the certified values. The values for Cr were also within the range of certified values (Table 4). Detection limits for Mn using F-AAS and Zeeman GF-AAS, based on a 2.0 g sample in a 20 ml final volume, were 0.15 mg kg^{-1} (ppm) and 1.10 $\mu g\ kg^{-1}$ (ppb), respectively. The detection limit for Cr using Zeeman GF-AAS, based on the same sample volume, was 1.0 $\mu g\ kg^{-1}$. These detection limits could be reduced by increasing the weight of the digested sample in order to improve the sensitivity of the methods.

Table 4. Comparison of HNO_3–H_2SO_4 digestion with and without the addition of HF for Cr analysis using Zeeman GF-AAS

Material	This study (mean ± SD)		Certified value
	With HF	Without HF	
Brewer's Yeast 1569	2.0 ± 0.1 (4)[a]	1.6 ± 0.1 (4)	2.12 ± 0.05
Tomato Leaves 1573	4.1 ± 0.6 (5)	4.3 ± 0.5 (7)	4.5 ± 0.5
Multigrain bread	17.2 ± 1.2 (6)	17.1 ± 0.8 (4)	
Lettuce	1.2 ± 0.1 (4)	1.2 ± 0.2 (4)	

[a]Number of samples analysed in parentheses.
All concentrations are expressed in $\mu g\ g^{-1}$.

Table 5. Manganese and chromium content in selected foods (wet weight)

Food groups	Manganese (mg kg^{-1})		Chromium (ng kg^{-1})
	n[a]	Mean ± SD	Mean ± SD
Breads			
Multigrain	7	17.0 ± 0.9	88.1 ± 9.0
Wholemeal	6	16.4 ± 0.3	78.9 ± 5.2
White	8	7.5 ± 0.2	34.0 ± 4.4
White rice (boiled)	5	7.0 ± 0.4	30.0 ± 3.5
Pasta (boiled)	6	1.3 ± 0.3	< LD[b]
Biscuits/cakes			
Cream	4	1.4 ± 0.2	23.0 ± 2.7
Chocolate	10	10.2 ± 0.7	30.5 ± 6.7
Scone	5	5.2 ± 2.5	42.2 ± 10.4
Muesli bar	4	22.0 ± 2.7	42.3 ± 10.0
Breakfast cereals			
Rice bubbles	4	2.5 ± 1.1	25.3 ± 2.7
Wheetbix/Vitabrits	4	26.0 ± 2.8	45.0 ± 3.5
Branflakes	3	55.0 ± 7.5	39.0 ± 7.6
Cornflakes	4	1.0 ± 0.2	58.4 ± 5.0
Meat/eggs			
Beef steak	6	0.52 ± 0.2	49.0 ± 1.8
Lamb chop	2	0.36	30.0
Sausages	4	1.2 ± 0.3	32.0 ± 1.4
Ham	5	2.0 ± 0.2	26.4 ± 2.7
Cooked chicken	6	0.19 ± 0.01	12.2 ± 5.0
Boiled egg	4	< LD	9.0 ± 1.4
Milk products			
Skim milk	4	0.4 ± 0.2	6.7 ± 1.5
Cheese	5	1.1 ± 0.2	95.0 ± 29.2
Yoghurt	3	0.26 ± 0.05	14.3 ± 4.0
Ice cream	5	< LD	< LD
Cream	3	< LD	13.3 ± 6.0
Butter	3	< LD	< LD
Margarine	3	< LD	< LD
Vegetables			
Roasted potato	5	0.9 ± 0.06	19.0 ± 2.2
Peas (frozen)	4	6.0 ± 1.2	28.3 ± 3.5
Bean (boiled)	4	3.4 ± 0.4	5.3 ± 1.6
Tomatoes	6	2.0 ± 0.1	30.0 ± 2.1
Carrot (boiled)	6	1.5 ± 0.1	13.0 ± 2.3
Pumpkin (boiled)	4	0.9 ± 0.2	16.0 ± 2.2
Cauliflower (boiled)	4	1.1 ± 0.2	6.3 ± 1.3
Broccoli (boiled)	3	1.2 ± 0.1	8.0 ± 2.0
Lettuce	5	1.3 ± 0.1	9.2 ± 1.3
Zucchini	3	1.3 ± 0.3	6.3 ± 1.2
Fruits			
Orange	4	0.4 ± 0.1	6.3 ± 1.2
Apple	4	0.5 ± 0.1	19.3 ± 3.3
Pear	5	0.8 ± 0.1	12.6 ± 1.8
Banana	5	3.3 ± 0.9	5.2 ± 1.3
Grapes	3	0.6 ± 0.1	4.3 ± 1.2
Pineapple (canned)	2	1.5	21.3
Rock melon	4	0.4 ± 0.1	9.8 ± 1.5

[a]n, number of samples analysed.
[b]LD, limit of detection of the method (refer to text for values of LD).

Levels of Mn and Cr in foods

Table 5 summarises results obtained when these validated analytical methods for analysis of Mn and Cr were applied to selected foods.

It can be seen (Table 5) that cereals and cereal products are the richest food sources of both Mn and Cr. Levels are highest in wholemeal compared to highly refined products. Particularly high levels of Mn, for instance, were recorded in wheat- and wheat bran-based breakfast cereals. Similar results have been reported in the UK by Wenlock *et al.* (1979) (Table 6). Cereal products have also been shown to contain high levels of Cr and can be a good source of Cr daily intake (Anderson *et al.*, 1988).

While relatively high levels of Cr were detected in certain meats, other than chicken, these were lower than the concentrations reported by others, including Farre and Lagarda (1986) in Spanish foods (Table 7). These differences may reflect differences in animal feeding practices in Australia compared to other countries. In the case of Mn, relatively low levels were found in meat products. Low levels of Mn in meats have also been reported for other countries (Table 6).

The lowest levels of both Mn and Cr in this study were found in fruits and vegetables. Although levels of Cr reported here are considerably lower than those reported by Smart and Sherlock (1985) in the UK, they are generally similar to levels in Spanish (Farre & Lagarda, 1986) and Swedish fruits and vegetables (Jorhem & Sundstrom, 1993) (Table 7). Wide variations of Cr levels in fruits and vegetables could be the results of environmental contamination, particularly when crops were growing in the vicinity of heavy agricultural activities and the use of sewage sludge as composts and fertilisers (Alegria *et al.*, 1990). Low levels of Mn in these foods have also been reported in other countries (Table 6).

Milk and milk products (Table 5) contained relatively low levels of Cr and Mn and they are generally considered to be poor sources of both elements. However, there is an exception in the case of Cr content in cheese. The higher levels found in this foodstuff may be due to pick up of adventitious Cr from stainless steel processing equipment (Reilly, 1991). Toepfer *et al.* (1973) have also found higher levels of Cr in US processed cheese.

Table 6. Reported content of manganese (mg kg^{-1}) in selected foods by other investigators

Food type	Wenlock *et al.* (1979)	Jorhem & Sundstrom (1993)
Wheat bran	—	118 (86–145)[a]
Wheat flour (extracted)	—	5.9 (2.6–20)
Wholemeal bread	24 (22–26)	—
White bread	4.1 (3.1–5.6)	—
White rice	8.7	—
Cornflakes	0.8 (0.7–0.9)	—
Beef steak	0.6 (0.4–0.8)	0.093 (0.049–0.14)
Ham	0.5	—
Pork	—	0.12 (0.058–0.33)
Lamb chop	0.3	—
Cooked chicken	0.3	—
Cooked egg	0.5 (0.4–0.8)	—
Cheese	0.3 (0.2–0.3)	—
Potato	1.2 (0.7–1.9)	1.9 (1.0–2.6)
Peas	2.6(1.6–1.9)	2.1 (2.1–2.2)
Chick peas	—	30 (29–30)
Bean (boiled)	1.6 (1.0–2.4)	—
Bean (green)	—	1.8 (1.4–2.2)
Bean (brown)	—	12 (12–12)
Cooked carrot	—	0.92 (0.32–2.4)
Tomato	0.9	1.0 (0.94–1.1)
Lettuce	—	1.5 (0.65–4.5)
Boiled cauliflower	2.7 (2.0–3.1)	—
Orange	0.3 (0.2–0.5)	—
Apple	1.0	0.34 (0.23–0.67)
Pear	—	0.49 (0.46–0.54)
Banana	10.2 (1.9–19)	1.7 (0.67–2.6)
Pineapple	2.3	—

[a]Values in parentheses indicate range of Mn concentration in food.

CONCLUSIONS

A mixture of HNO_3–H_2SO_4–$HClO_4$ or HNO_3–H_2SO_4 for the digestion of food samples for Mn analysis was found satisfactory. The use of HNO_3–H_2SO_4 mixture without the addition of HF for the digestion of food

Table 7. Reported content of chromium (ng kg^{-1}) in selected food by other investigators

Food type	Smart & Sherlock (1985)	Farre & Lagarda (1986)	Jorhem & Sundstrom (1993)
Wheat bran	—	—	18 (6–30)[a]
Wheat flour (extracted)	—	—	7 (2–15)
Wholemeal bread	—	—	—
White bread	—	118	—
Spaghetti	—	126	—
Beef steak	—	91	< 10 (< 10–20)
Pork	—	—	14 (< 10–440)
Cooked chicken	—	66	—
Cooked egg	—	23	—
Cheese	—	43	—
Potato	150	30	6 (2–14)
Peas	42	—	4 (3–4)
Chick peas	—	—	51 (48–54)
Bean (green)	—	—	22 (6–38)
Bean (brown)	—	—	44 (37–51)
Cooked carrot	150	27	3 (1–6)
Tomato	240	9	3 (2–4)
Lettuce	170	65	11 (5–16)
Orange	—	17	—
Apple	—	24	2 (< 1.0–3)
Pear	—	57	3 (2–3)
Banana	100	38	1 (< 1.0–2)

[a]Values in parentheses indicate range of Cr concentration in food.

samples for Cr analysis was also satisfactory with good reproducibility. The addition of HF to acid mixture for the analysis of Cr was found unnecessary, and this will help to minimise problems of contamination and high blank.

Although the foods do not represent the full range available, they do include examples of all categories normally consumed in Australia. Consequently, the results will permit reliable estimates to be made probably for the first time of dietary intakes of the two elements in Australia.

It is clear from these findings that cereal products contain the highest concentration of Mn and Cr. On the whole, and especially for Mn, the levels found in this study were comparable with the values reported by Wenlock *et al.* (1979). The levels of Cr in individual foods found in this study were much lower than the previously reported values. A decline in Cr levels in individual foods has also been shown by Jorhem and Sundstrom (1993). Anderson and Kozlovsky (1985) have also expressed the view that, as the analytical techniques and instrumentation improved and more attention was paid to the validity of the analysis and the problem of contamination, the levels reported in diets would decrease. They showed dramatic variations and decreasing levels of reported Cr daily intake over the years.

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