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Food Chemistry 68 (2000) 37–39

Food Chemistry

www.elsevier.com/locate/foodchem

# Manganese in pineapple juices

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Received 1 March 1999; received in revised form; accepted 24 May 1999

**Abstract**

Levels of manganese (15–22 ppm) in commercial pineapple juices were found to be consistently much higher than those of Cr, Fe, Ni or Cu and much higher than in other common fruit juices. The manganese levels in juice extracted from fresh Australian pineapples were variable, with some high and some low levels. Most of the manganese was found in the filtered juice and little in the pulp retained on an 0.4 micron filter. Electron paramagnetic resonance spectroscopy shows that most of the manganese is present as the $Mn(H_2O)_6^{2+}$ species. The remainder is released in this form if the juice is acidified to pH 1. © 1999 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

During a routine survey of the levels of some transition metals in commercial fruit juices, we observed an anomalously high level of manganese in pineapple juice (Fig. 1). Further investigation has revealed that pineapple appears to concentrate manganese to a much greater extent than do other juice fruits. A survey of the literature revealed that this phenomenon has been observed previously, (Cámara, Díez & Torija, 1995; Falandysz & Kotecka, 1992; Pilando & Wrolstad, 1992) but the presence of high levels of manganese in pineapple fruit has not until recently been presented in standard texts and articles (Greger & Malecki, 1997; Py, Lacoeuilhe & Teisson, 1987).

Manganese is an essential trace element, but human requirements and optimal levels have not been well established (Greger & Malecki, 1997). Furthermore the nutritional bioavailability of manganese is uncertain (Kies, 1987). In this work we have measured the overall level of manganese in commercial pineapple juices and in juice from fresh fruit and have made a preliminary investigation of the form of the manganese present by electron paramagnetic resonance spectroscopy.

## 2. Materials and methods

### 2.1. Samples

Commercial pineapple juices were purchased in Sydney, Australia and in the UK (one sample). Fresh pineapples were purchased from different shops in Sydney at different times of the year. The skinned fruit was ground with a pestle in a mortar and the juice extracted by decantation.

The juice samples were prepared for analysis in three different ways:

1. A 10 ml sample was centrifuged at 15,000 rpm for 30 min and then filtered through an 0.4 μm membrane filter.
2. A second 10 ml sample was evaporated to dryness and then digested with concentrated sulfuric and nitric acids.
3. A third 10 ml sample was centrifuged and filtered as in (1) and then digested as in (2).

If the Mn levels were above the calibration limit of 5 ppm, the samples were diluted by a factor of 5 with water or 0.1 M HCl.

### 2.2. Methods

Atomic absorption analyses for Mn were performed with a Varian SpectrA 800 spectrometer at 279.5 nm.

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PII: S0308-8146(99)00149-1

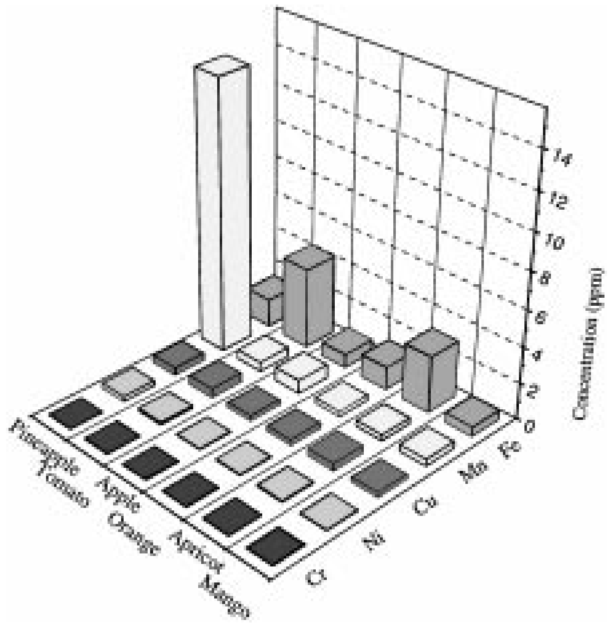


Fig. 1. Concentrations (ppm) of some transition metals found in commercial fruit juices.

EPR spectra were recorded with a Bruker EMX spectrometer at room temperature. Common standard solutions of 1.0 to 5.0 ppm of Mn were prepared by the dissolution of manganese metal in 0.1 M HCl.

## 3. Results and discussion

The concentrations of manganese found by FAAS and EPR in various pineapple juice samples under different treatment conditions are shown in Table 1. The first five samples listed are commercial juices; the remaining eight are from different fresh pineapples.

The first column of results shows the total Mn content obtained by acid digestion of the samples. The commercial juices contained between 15 and 22 ppm of Mn, and the fresh pineapple between 2 and 22 ppm. It is apparent that the five commercial juice samples listed first have much higher levels of manganese than most of the eight fresh juice samples. Of the latter, only sample F7 shows a high level of 22 ppm, and sample F6 contains 10 ppm. It might be thought that this could reflect metallic contamination from processing the relatively acidic juice, but the associated iron levels are not high, so this source of Mn in the processed juices is excluded. The commercial juices were all single-strength beverages, not concentrates. The difference then could just reflect geographic variations in the sources of the pineapples for the two different markets — fresh fruit and commercial juice. Alternatively, it could reflect the different extraction procedures used by the industry and in the laboratory.

Comparing the first two columns of results, the digested whole juice has the highest observed levels, as expected, for the digestion procedure should release all of the manganese contained in the sample. Little manganese is in the pulp retained by a 0.4 micron filter, for the levels found in the digested filtrate are only slightly lower than those of the digested whole juice. Finally, from the next colum, it is observed that the values measured for direct measurement of the filtered juice, without destructive digestion, are at least two-thirds of those obtained by digestion. This implies that most of the manganese is quite loosely bound.

The epr results indicate this more clearly. In the digested whole juice, the manganese displays a six-line epr signal identical with that of the $Mn(H_2O)_6^{2+}$ standard, indicating that the manganese under these treatment conditions has been converted to this Mn(II) state. Also, as expected, the concentrations observed by epr are the same within the experimental errors as those measured by atomic absorption spectroscopy. There is a similar relationship with the intensity of the epr signals

Table 1
Concentrations (ppm) of Mn in various pineapple juices

| FAAS | | | | EPR | | |
|---|---|---|---|---|---|---|
| Sample | Digested whole juice | Digested filtrate | Direct filtrate | Digested whole juice | Digested filtrate | Direct filtrate |
| A1 | 16 | 14 | 9.1 | 15 | 12 | 11 |
| A2 | 15 | 15 | 10 | 13 | 13 | 11 |
| B1 | 18 | 15 | 14 | 20 | 13 | 15 |
| B2 | 17 | 16 | 12 | 15 | 15 | 14 |
| C | 22 | 21 | 20 | 21 | 21 | 14 |
| F1 | 7.1 | 6.5 | 5.5 | – | – | – |
| F2 | 2.4 | 2.3 | 1.7 | 1.9 | 1.7 | 2.0 |
| F3 | 2.7 | 2.3 | 1.9 | 3.2 | 2.3 | 2.0 |
| F4 | 1.8 | 1.6 | 1.2 | 1.3 | 1.0 | 1.2 |
| F5 | 1.8 | 1.6 | 1.7 | 2.6 | 2.3 | 1.7 |
| F6 | 9.8 | 11 | 11 | 8.9 | 10 | 4.5 |
| F7 | 22 | 23 | 23 | 19 | 17 | 9.5 |
| F8 | 2.2 | 2.2 | 1.3 | 1.7 | 1.7 | 1.1 |

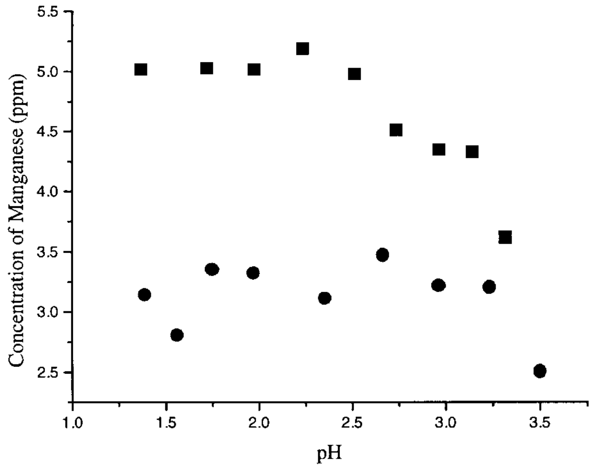


Fig. 2. pH dependence of EPR signal of $Mn(H_2O)_6^{2+}$ for fresh (■) and commercial (●) pineapple juices.

in the digested filtrate. Of more significance, the epr measured on the acidified filtrate has again at least two-thirds of the intensity of the signals of the digested samples. This indicates that the Mn is present in the natural juices, largely as the unbound $Mn(H_2O)_6^{2+}$ form. Only in the two fresh juice samples, with higher levels (F6 and F7), are the epr signals from the undigested filtrate significantly lower than those from the digested treatments. This suggests that, in these samples, part of the Mn may well be bound in some complex form, or in a different oxidation state, which is epr silent.

To confirm this inference, an additional set of experiments was undertaken. The epr signals were measured as the pineapple juice samples were acidified from their natural pH of about 3.5 to pH 1. The results are presented in Fig. 2. For the commercial juice there was not much difference but, for the fresh juice, there was a clear increase in the signal intensity from above pH 3 to below pH 2. This implies that a fraction (about one-third) of the Mn in the fresh juice is not epr-observable, while the remaining two-thirds is in the form $Mn(H_2O)_6^{2+}$. As the acidity is increased, this bound form is released as $Mn(H_2O)_6^{2+}$. The difference is much less marked in the commercial juices, which suggests that, during the preparation or storage of the commercial juices, the Mn is released by some other process, possibly enzymic.

The high levels of manganese probably reflect the acidic soil conditions in which pineapple is cultivated. The optimum pH has been found to be between 4.5 and 5.5 (Py et al., 1987). Further investigations beyond this preliminary study are required to correlate the managanese levels with soil characterisitcs of the various growing locations. Manganese deficiency in pineapple plants appears to be uncommon, but soils high in manganese can lead to iron deficiency. It has been reported that immature pineapple pulp contains as much as 40 ppm of manganese, but that this level declines markedly at maturity (Kermasha, Barthakur, & Alli, 1987). Of more significance, the present results confirm that pineapple products in a diet could contribute a large fraction of the daily human manganese intake and that the manganese is present in what is thought to be an assimilable form (Kies, 1987).

## Acknowledgements

T.N.Q. acknowledges AusAID for the support of an Australian Sponsored Training Scholarship during the course of which this work was conducted. We acknowledge helpful correspondence with Dr. Peter Lawson of Central Queensland University.

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