Atomic Absorption Full Method
Sn in Canned Fruit Juice

Key Words

• Tin

• Fruit Juice

• Canned Fruit Juice

• QuadLine Background Correction

• Graphite Furnace

• Atomic Absorption

• Extended Lifetime Cuvettes

• Matrix Modification

Introduction

Inorganic tin and its compounds are poorly absorbed in the intestinal tract and lasting harmful effects have not been documented. However even small amounts of the metal can adversely affect the flavour and storage properties of food products.

The metal is introduced as a contaminant during processing of food products and can accumulate during storage due to leaching from the containers.

The United Kingdom food regulations permit a maximum guideline limit of 250 mg/kg in canned foods(1). However improvements to the processing and use of new materials for canning mean food manufacturers are required to measure significantly lower concentrations.

The traditional flame atomic absorption spectrometric determination of tin is relatively insensitive, and accurate quantification at low concentrations is difficult.

Tin can be successfully determined by Graphite Furnace Atomic Absorption Spectrometry using an accurate background correction system provided care is taken to minimise losses during the program cycle.

Analytical range

A method for the determination of tin in canned fruit juices is presented. The 3 sigma method detection limit is 11 µg/L in the original sample, and concentrations up to 500 µg/L can be measured using the method described. Samples with higher levels of tin could be analysed after dilution.

Principle

Tin is extracted from the sample with hydrochloric acid and is determined by direct calibration against aqueous standards with Quadline background correction. Ammonium nitrate is used as a matrix modifier with conventional off-the-wall atomisation from an Extended Life Cuvette.

Method

Reagents:

Hydrochloric acid (Spectrosol grade).
Tin master standard (1000 mg/L Spectrosol or equivalent).
Ammonium nitrate (Aristar grade or equivalent).

All reagent examples available from:

Fisher Scientific
Bishop Meadow Rd
Loughborough,
LE11 5RG
UK.

Sample collection

Tin can be easily extracted from food products by hydrolysis with hydrochloric acid(2,3). Samples should be well mixed by shaking before analysis.

Pipette 20.0 mL of fruit juice into a 100 mL beaker and add 10 mL of hydrochloric acid. Heat the mixture to boiling point and after allowing it to cool transfer it to a 100 mL volumetric flask and make up to the mark with deionised water. An aliquot of this solution should be centrifuged prior to analysis, and the clear supernatant transferred to the autosampler cup.

Method development

Standard solutions containing 25, 50, and 100 µg/L of tin in 10 % v/v hydrochloric acid and an acid blank were prepared. A canned orange juice sample spiked at 125 µg/L was used for the method development experiments.

Ridged Extended Lifetime Cuvettes were used throughout.

Thermo
S C I E N T I F I C

Spectrometer

Sn juice (Sn)

Measurement Mode:	Absorption
Number of Resamples:	3
☐ Fast Resamples	
Measurement Time: (s)	3.0
Wavelength: (nm)	224.6
Lamp Current: (%)	90
Bandpass: (nm)	0.5

☐ High Resolution
Background Correction: D2 Quadline

Flier Rejection
☐ Use Flier Rejection
Rejection Limit: (%) 95

RSD Test
☐ Use Test
If RSD greater than 0 %
AND signal greater than 0.1 Abs
Then Flag and Continue

☐ Optimise Spectrometer Parameters
Signal: Transient Height

Transient Peak Measurement
Measure From (s): 0.00 To: 3.00

Furnace

Sn juice (Sn)

Cuvette: ELC
Injection Temperature: (°C) 0
Programme Time: (secs) 124.5

Furnace Programme

	Temp (°C)	Time (s)	Ramp (°C/s)	Gas Type	Gas Flow	RD	RS	TC	NL
1	80	40.0	20	2 Inert	0.2 L/min				
2	100	10.0	2	2 Inert	0.2 L/min				
3	450	15.0	20	2 Inert	0.2 L/min				
4	800	15.0	50	2 Inert	0.2 L/min				
5	2500	3.0	0	2 Inert	Off	✓	✓		
6	2700	3.0	0	2 Inert	0.2 L/min				
7	0	0.0	0	2 Inert	Off				
8	0	0.0	0	2 Inert	Off				
9	0	0.0	0	2 Inert	Off				

☐ Clean Cuvette if sample greater than: ___ Abs

Sampling

FS95

Sample
Sample Preparation: None
Sample Volume: (µL) 10.0
Injections: 1
Intelligent Dilution Threshold (%): 100
Working Volume: (µL) 10.0
Standard Preparation: Manual
Standard Additions: None

☐ Slow Solution Uptake
☐ Slow Solution Injection
☐ Sampling Delay
☐ Automatic Spike
Spike Volume (µL): 20.0
Washes: 1

Matrix Modification

	Name	Volume (µL)	Order	Method
1	Ammonium nitrate	10.0	1	Wet
2		20.0	2	None
3		20.0	3	None
4		20.0	4	None
5		20.0	5	None
6		20.0	6	None

Volumes... Reagent Details...

☐ Wash Autosampler if sample greater than: ___ Abs

Calibration

Sn juice (Sn)

Method: Normal: Segmented Curve Fit
☐ Use Stored Calibration
Concentration Units: ng/mL
Standards: 3   Default Ratios

Standard Concentrations
Master Standard Conc: 100

1	25.000	6	0.000
2	50.000	7	0.000
3	100.000	8	0.000
4	0.000	9	0.000
5	0.000	10	0.000

Scaling Factor: 1
Scaled Units: ng/mL

Calibration Checks
Acceptable Fit: 0.995

Excess Curvature Limits
From: (%) - 10
To: (%) + 40
Rescale limit: 10 %

If any calibration checks fail:
Flag and Continue
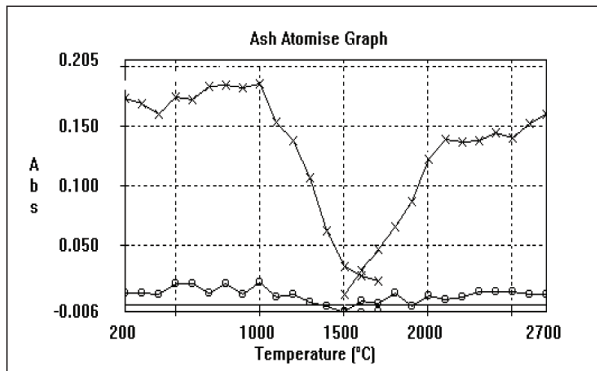
Figure 1: Analysis parameters

Figure 2: Ash/atomise plot for orange juice with matrix modifier

For these reasons 10 µL of a 2 % m/v solution of ammonium nitrate was used as a matrix modifier. This has the advantage of volatilising the chloride present in the sample as ammonium chloride while stabilising the tin.

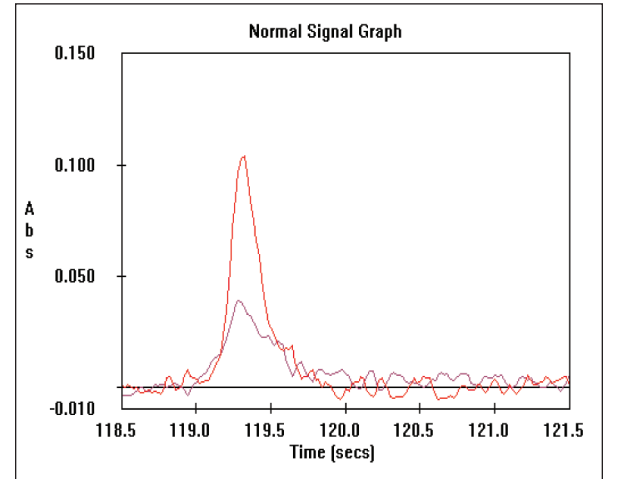Figure 3: Correction with QuadLine background correction

Figure 4: Correction with Zeeman background correction

An ash/atomise plot for the spiked juice was automatically generated (figure 2).

This showed that the tin was stable up to a temperature of 1000 °C in the presence of the matrix modifier, while optimum signals were obtained by atomising at 2500 °C. Clean well defined peak shapes were obtained with minimal background signals for both QuadLine (figure3) and Zeeman (figure 4) background correction systems, both of which were capable compensating accurately for the small residual background. The Quadline system was used because of the superior sensitivity and baseline noise levels obtained.
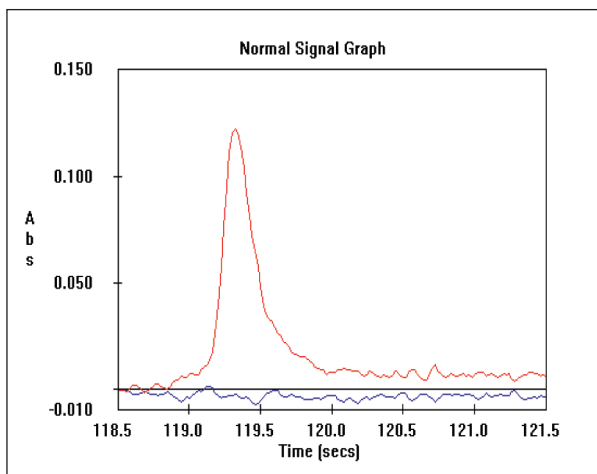
Method validation

Two samples of canned orange and pineapple juice were spiked at 125 and 250 µg/L, and prepared and analysed by the proposed method. Recoveries of the spikes were calculated, as shown in Table 1.

Sample	Orange Juice	+125 µg/L	+250 µg/L
Tin found (µg/L)	52	174	285
Recovery (µg/L)		122 98 %	233 93 %

Sample	Pineapple Juice	+125 µg/L	+250 µg/L
Tin found (µg/L)	31	158	268
Recovery (µg/L)		127 102 %	237 95 %

Table 1: Validation spike recovery experiment results

To check for matrix effects the standard additions lines were plotted over the aqueous calibration line. This is shown in figure 5.

To assess the overall precision of the method ten replicate measurements were taken of two samples and two spikes. Each sample result was the mean of three resamples. The results are shown in figure 6.

Figure 5: Standard additions experiment results

Results

The results of the recovery experiment are summarised in table 1 and figure 5. The calibration lines are parallel indicating a freedom from matrix interferences, and complete recoveries of the spikes were obtained.

The results of the validation experiment are summarised in figure 6 and indicate that the method gives stable results with no significant drift.

The characteristic mass (the mass required to give a signal of 0.0044 absorbance.seconds in peak area or 0.0044 absorbance units in peak height) for tin measured under the method conditions was found to be 12.2 pg for height measurement and 22.0 pg for area measurement.

The canned juices were found to have concentrations of 52 and 31 µg/L for the orange and pineapple respectively. The unspiked juice sample used for the validation experiment gave a mean result of 44µg/L with a standard deviation of 3.7 µg/L, giving a 3sigma detection limit for the method of 11 µg/L of tin in the original sample.

Conclusions

A simple method for the routine determination of tin in canned fruit juices is presented. Use of matrix modification with ammonium nitrate allows calibration against simple aqueous standards, and the minimal residual background signal is easily corrected by the Quadline background correction system.

Off the wall atomisation was entirely suitable for this analysis, giving excellent sensitivity and detection limits, while the Extended Life Cuvettes ensure a long term reproducible signal even with the high acid concentration of the sample digest.
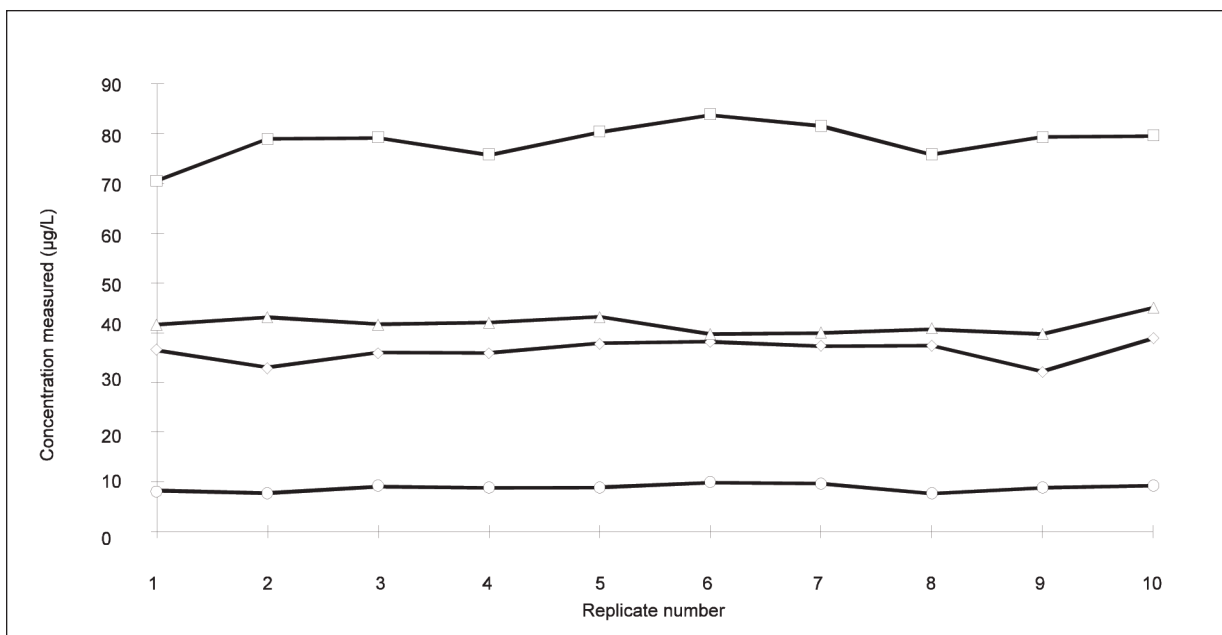
Figure 6. Validation experiment results

References

(1) Food RA Guide to the UK Regulations, 2nd edition, Jan 1981, page 58.

(2) Simpson, G. R., Blay, R. A., Food Trade Rev., 36(8), 35, 1966.

(3) Szarski, P., Food Tech, 216, May, 1971.