

Atomic Absorption Analysis of Heavy Metals in Factory Water and Granulated Sugar

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Introduction

In the last two years, increased attention has been focused on a group of pollutants known as heavy metals. A group of environmental scientists, in constructing an index of priorities in handling pollution, has ranked heavy metals second only to pesticides for present environmental problems (3)². For the future, heavy metals lead the priority list. This growing interest in heavy metal contaminants has prompted national, state, and local health agencies to increase their surveillance activity in consumer products. One phase of this increased activity has resulted in the collection of products for human consumption and analyzing for trace metals such as arsenic, mercury, lead, copper, and zinc.

Although regular granulated sugar is considered one of the purest commercial food products known, Spreckels research initiated a program to determine those elements which might be present in detectable limits using the latest techniques for analyses in submicrogram ranges.

Heavy metals in sugar have been determined using polarographic (10, 15) and emission spectrographic (4) methods. With the exception of copper, iron, and zinc the quantities of heavy metals detected in sugar were in the submicrogram range. Copper, iron, and zinc were generally found at the microgram level. Mercury apparently has not been reported in refined sugar.

Recently, atomic absorption has been applied to the analyses of various products of the sugar industry (2, 7, 12). Carpenter and Bichsel (2) have used this technique for determining Na, K, Mg, Ca, Cu, and Fe in diffusion supply water, process juices, molasses, and white sugar. The speed and simplicity of atomic absorption make this technique particularly well suited for the determination of trace metals in water.

This report describes analytical procedures based on atomic absorption techniques for determination of arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, and zinc in factory water and granulated sugar.

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²Numbers in parentheses refer to literature cited.

Experimental Procedure

Reagents

Reagent grade chemicals and deionized distilled water were used throughout this investigation.

Glassware used for the determination of arsenic was soaked with HCl, while glassware used for other determinations was soaked with aqua regia for 2 hours and rinsed with distilled water and deionized water.

Standard stock solutions (200 $\mu\text{g/ml}$) of Cd, Cr, Cu, Fe, Pb, Mn, and Zn were prepared in 0.25 N HCl. Portions of these stock solutions were mixed together and diluted to working standards with 0.25 N HCl. Sufficient amounts of NaCl were added to each multielement standard solution to contain 50 $\mu\text{g/ml}$ of sodium. A blank was prepared similarly. The concentrations of each element in different working standard solutions are shown in Table 1.

Standard stock solutions (100 $\mu\text{g/ml}$) of As and Hg were prepared in 4.5 N HCl and in N H^2SO_4 , respectively. The arsenic working standard solution (0.20 $\mu\text{g/ml}$) was prepared fresh daily by diluting a portion of the stock solution with 4.5 N HCl, while the mercury working standard (0.020 $\mu\text{g/ml}$) was also made up fresh daily in N H_2SO_4 and 0.25% KMnO_4 .

Table 1.—Concentration of various metals in working standard solutions.

Working Standard	Cd	Cr	Cu	Metal in $\mu\text{g/ml}$			Mn	Zn	Na
				Fe	Pb				
1	0.020	0.10	0.10	0.10	0.020	0.050 ^a	0.010	50	
2	0.050	0.20	0.20	0.20	0.050	0.10	0.020	50	
3	0.080	0.40	0.40	0.40	0.080	0.20	0.040	50	

Apparatus

All data were obtained using a Perkin-Elmer Model 403 atomic absorption spectrophotometer, equipped with a Honeywell Elektronik 193 strip chart recorder. A Deuterium Background Corrector was employed in the determination of arsenic. Both single and multi-element (Cu-Fe-Mn-Zn) hollow cathode lamps manufactured by Perkin-Elmer were used. A standard burner head (4 in) was used in conjunction with an air-acetylene flame or argon-hydrogen entrained air flame, while a nitrous oxide burner head was employed for the nitrous oxide-acetylene flame. Relevant operating parameters are listed in Table 2.

Table 2.—Operating parameters.

	Element								
	As	Cd	Cr	Cu	Fe	Pb	Hg	Mn	Zn
Wavelength, Å	1937	2288	3579	3247	2483	2833	2537	2795	2138
Slit opening, mm	1	1	0.3	1	0.3	1	1	1	1
Recorder response	1	3	3	2	3	3	2	2	2
Type of flame	Ar	Air	N ₂ O	Air	Air	Air		Air	Air
	H ₂	C ₂ H ₂	C ₂ H ₂	C ₂ H ₂	C ₂ H ₂	C ₂ H ₂	none	C ₂ H ₂	C ₂ H ₂

Determination of Cd, Cr, Cu, Fe, Pb, Mn, and Zn

Sample Preparation for Factory Water

A 500 ml of millipore filtered water sample is acidified with 5 ml of concentrated HNO₃ and concentrated to 100 ml by evaporation. Duplicate blanks consisting of deionized water and HNO₃ are prepared together with the sample in a similar manner.

Sample Preparation for Granulated Sugar

The sulfated ash from 100 g of granulated sugar is dissolved in 4 ml of hot 6 N HCl and diluted to exactly 25 ml.

Atomic Absorption Analysis

Aspiration of the standard, blank, and sample solutions is carried out with operating parameters as listed in Table 2. A calibration curve is prepared for each element from the recorded absorption signals of the working standards.

Determination of mercury

Sample Preparation for Factory Water

One milliliter of 18N H₂SO₄ followed by 1 ml of 5% KMnO₄ solution are added to 50 ml of water sample. The mixture is boiled for about one minute, cooled, transferred into a 125-ml gas-washing cylinder and diluted to a volume of 60 ml. Three standards containing 0.020, 0.040, and 0.060 µg Hg together with two blanks are prepared in the same manner.

Sample Preparation for Granulated Sugar

Seventy-five milliliters of concentrated HNO₃ is added to a 250-ml Erlenmeyer flask containing 3 g of granulated sugar. The contents of the flask are heated slowly and at the first appearance of NO₂ heating is stopped. After the reaction has subsided, the mixture is digested until the volume of the solution is reduced to about 15 ml. On cooling, 25 ml of concentrated HNO₃ is added, and the mixture is again reduced to 15 ml. At this point, the sample is slightly yellow and turns colorless on cooling. Any sign of NO₂ remaining in the flask will require repetition of the addition of HNO₃ and digestion.

The digested sample is transferred into a 125-ml gas washing cylinder and the volume is diluted to 60 ml. Three mercury standards and two blanks are prepared in the same manner.

Flameless Atomic Absorption Analysis

The apparatus used in this study was similar to the one described by Mittelhauser (13), except a bottle normally used for condensing water vapor was eliminated.

The apparatus is assembled as shown in Figure 1. Tygon tubing is used for connection of various glassware. A quartz-windowed gas cell, 10 cm path length, held in a plexiglass holder is placed on top of a standard burner head. The absorption cell is then adjusted vertically and horizontally to give maximum absorption. The flow rate of air used to sweep the mercury vapor through the cell is adjusted to 1.5 liters/minute. Optimum air flow varies with the design of each apparatus. However, a flow rate that produces maximum absorption without causing excessive foaming is recommended.

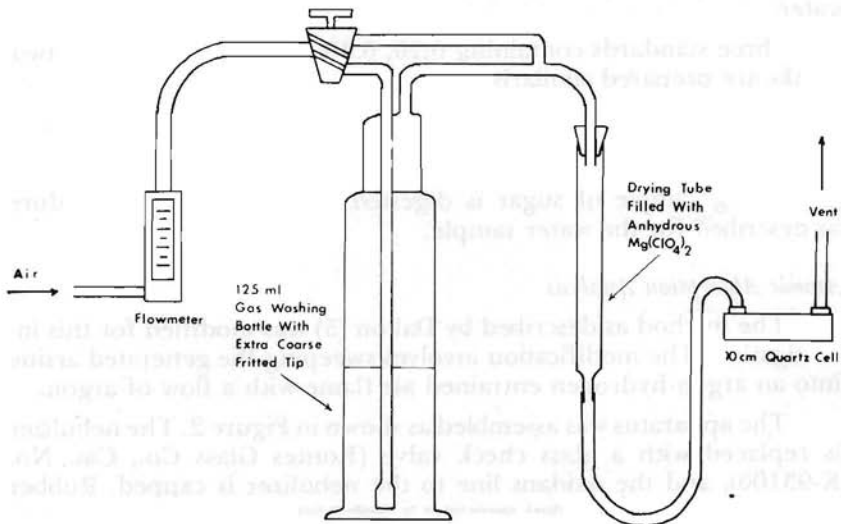


Figure 1.—Apparatus used for the reduction of mercury.

Two milliliters of a mixed sodium chloride-hydroxylamine hydrochloride solution (10% $NaCl$ -10% $NH_2OH \cdot HCl$) followed by 3 ml of 10% $SnCl^2$ in 0.5N H_2SO_4 are added to a sample solution. Immediately the cylinder is connected to the apparatus. The mercury vapor is swept through the absorption cell with air by turning the two-way stopcock from the bypass to the aeration position.

The resulting peak height as observed on a recorder chart is proportional to the mercury content. A calibration curve is prepared by plotting the peak heights of the standards minus the blank versus μg of mercury.

Determination of arsenic

Sample Preparation for Factory Water

In the absence of nitrate and organic materials, digestion of the water sample is unnecessary.

Fifteen milliliters of concentrated HNO_3 and 4 ml of concentrated H_2SO_4 are added to a 500 ml Kjeldahl flask containing 35 ml of water sample. The mixture is digested to fumes of SO_3 . Oxidizing conditions must be maintained at all times to avoid loss of arsenic. Whenever a mixture remains brown at the first sign of SO_3 , an additional 1-2 ml of HNO_3 is added and heating is continued until the solution no longer darkens. To expel any remaining oxides of nitrogen, 10 ml of a saturated ammonium oxalate solution is added. Again the mixture is heated to fumes of SO_3 and the heating is continued for five minutes.

The cooled, digested sample is then transferred into a 125 ml, 24/40 flat bottom flask. Twenty milliliters of concentrated HCl is added and the volume of the sample solution is diluted to 60 ml with deionized water.

Three standards containing 0.20, 0.40, and 0.60 μg As and two blanks are prepared similarly.

Sample Preparation for Granulated Sugar

A 5 g sample of sugar is digested using the same procedure as described for the water sample.

Atomic Absorption Analysis

The method as described by Dalton (5) was modified for this investigation. The modification involves sweeping the generated arsine into an argon-hydrogen entrained air flame with a flow of argon.

The apparatus was assembled as shown in Figure 2. The nebulizer is replaced with a glass check valve (Kontes Glass Co., Cat. No. K-93100), and the oxidant line to the nebulizer is capped. Rubber

Figure 2. Apparatus Used For The Generation Of Arsine.

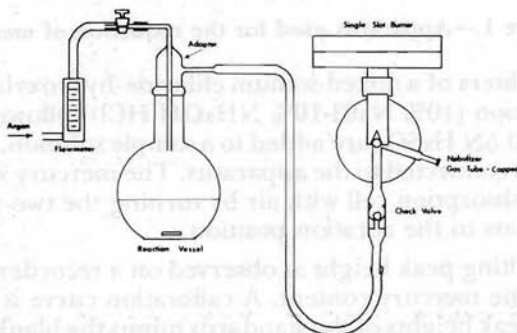


Figure 2.—Apparatus used for the generation of arsine.

tubing is used for connection of glassware. The following flow rates for the argon-hydrogen entrained air flame were found to be optimum: 10 liters/minute for argon and 7 liters/minute for hydrogen. The flow rate of argon used to sweep the arsine into the flame is adjusted at 0.9 liter/minute.

Two milliliters of 20% KI followed by 2 ml of 20% SnCl_2 are added to each sample, standard and blank solution. The mixture is thoroughly mixed and allowed to stand for about five minutes.

While the solution is being stirred, 10 g of zinc granules (40 mesh) is added and the adapter is immediately placed on the flask. The stop-cock is then turned to an open position, allowing the argon to flow into the reaction flask and sweeping the AsH_3 rapidly into an argon-hydrogen flame.

The area under the recorder tracing peak represents the quantity of arsenic. It is computed by multiplying the peak height times the width at half-height. A calibration curve is prepared by plotting the areas of the standards minus the blank versus μg of arsenic.

Results and Discussion

Chromium. Preliminary recovery experiments conducted with an air-acetylene flame disclosed that the recovery of chromium was less than quantitative.

Several publications have indicated that the determination of chromium by atomic absorption in an air-acetylene flame is strongly affected by the presence of a large number of elements (1, 6, 8, 16). Among elements reported interfering are Al, Cu, Fe, Co, Ti, Mn, Ni, Ag, and Mo. The chemical interferences are more severe in a reducing flame than in an oxidizing flame. Some of these interferences can be minimized by using a suppressing agent such as NH_4Cl (1, 6), $\text{K}_2\text{S}_2\text{O}_7$ (16), or Na_2SO_4 (8), or by using a nitrous oxide-acetylene flame (9, 11, 17).

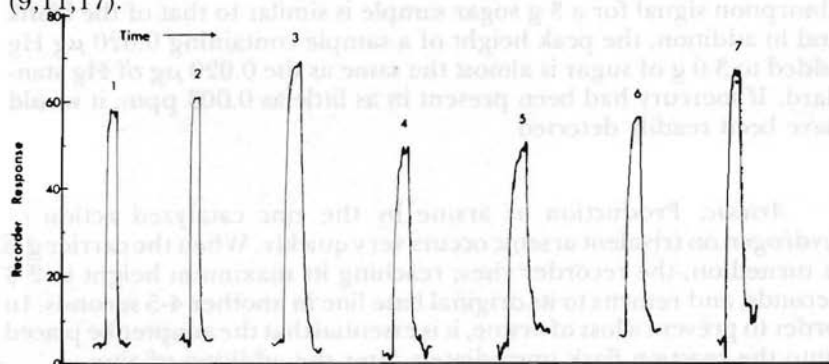


Figure 3. Recorder tracings of (1) 0.04 ppm Zn, (2) 0.4 ppm Cu, (3) 0.2 ppm Mn, (4) 0.4 ppm Fe, (5) 0.08 ppm Cd, (6) 0.08 ppm Pb, (7) 0.4 ppm Cr.

Figure 3.—Recorder tracings of 1) 0.04 ppm Zn, 2) 0.4 ppm Cu, 3) 0.2 ppm Mn, 4) 0.4 ppm Fe, 5) 0.08 ppm Cd, 6) 0.08 ppm Pb, 7) 0.4 ppm Cr.

Utilization of a nitrous oxide-acetylene flame appeared to be the simplest method of reducing chemical interferences without the danger of contaminating the sample. Consequently, a nitrous oxide-acetylene flame was used for all chromium determinations.

Figure 3 exhibits recorder tracings of absorption signals produced by standard Zn, Cu, Mn, Fe, Cd, Pb, and Cr solutions. Favorable signal-to-noise ratios are evidenced.

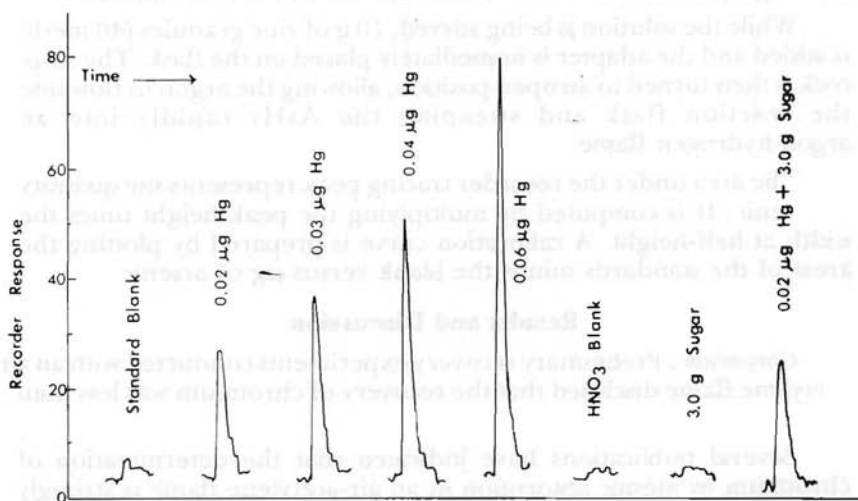


Figure 4.—Recorder tracings for mercury at 2537 Å using the flameless atomic absorption technique. Recorder response set at 2.

Mercury. Figure 4 shows recorder tracings of the absorption signal for mercury, measured at the 2537 Å resonance line. Note that the absorption signal for a 3 g sugar sample is similar to that of the blank and in addition, the peak height of a sample containing 0.020 µg Hg added to 3.0 g of sugar is almost the same as the 0.020 µg of Hg standard. If mercury had been present in as little as 0.003 ppm, it would have been readily detected.

Arsenic. Production of arsine by the zinc catalyzed action of hydrogen on trivalent arsenic occurs very quickly. When the carrier gas is turned on, the recorder rises, reaching its maximum height in 2-3 seconds, and returns to its original base line in another 4-5 seconds. In order to prevent a loss of arsine, it is essential that the adapter be placed onto the reaction flask immediately after the addition of zinc.

Experimental tests indicate that the rate of arsine formation is affected by the particle size of the zinc, the amount of zinc used, the concentration of hydrochloric acid and the volume of the final solution.

When peak heights were used to correlate the amount of arsenic in standards which had been treated as normal samples, results between two determinations differed by as much as 30%. However, if the area under the peak was used to represent the quantity of arsenic, the precision between determinations was significantly improved.

The area under the peak was calculated by multiplying the peak height times the width at half height. A six-power magnification comparator was used to measure the width to within ± 0.1 mm.

Table 3.—Comparison of methods used to evaluate absorption signal.

(Each sample contained 1.0 μg of Arsenic)		
No. Dctn.	By peak height, mm	By area, mm^2
1	92.0	221
2	88.5	212
3	122.0	207
4	94.0	197
5	124.0	198
	Σ	1035
	\bar{X}	207
Std Dev	S	10.0
Rel Std Dev	S_r	4.8%

Table 3 shows results obtained by measuring the peak height and by computing the area under the peak for five replicate determinations. By estimating the area under the peak, the relative standard deviation was calculated to be 4.8% at $1\mu\text{g}$ level.

Recovery of Various Elements. To establish the accuracy of various methods known amounts of Cd, Cr, Cu, Fe, Pb, Mn, Zn, As, and Hg were added to factory water and to granulated sugar and treated as normal samples. Determinations of original samples and samples with added metals were made in triplicate. The average recoveries of the above-mentioned elements are summarized in Table 4.

Table 4.—Recovery of various metals added to factory water and granulated sugar.

Metal	Factory water			Granulated sugar		
	μg Added	μg Recovered	% Recovery	μg Added	μg Recovered	% Recovery
As	0.50	0.52	104	0.50	0.51	102
Cd	5.0	5.0	100	1.0	1.0	100
Cr	20.0	20.5	102	5.0	4.9	98
Cu	50.0	49.1	98	3.0	3.2	107
Fe	20.0	20.7	104	3.0	3.1	103
Pb	3.0	3.0	100	1.0	1.0	100
Mn	5.0	5.1	102	3.0	2.9	97
Hg	0.050	0.050	100	0.030	0.028	93
Zn	5.0	5.2	104	0.50	0.51	102

These data demonstrate that the described methods are suitable for the determination of As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, and Zn in factory water and granulated sugar if present in detectable quantity.

Detection Limits

Using the standard sampling technique, *viz.*, aspirating solutions into a flame, the detection limit is defined as the concentration, in $\mu\text{g}/\text{ml}$, which gives a signal twice the size of the background noise(14). For other sampling techniques, the detection limit is the amount of metal, in μg , which produces a signal-to-noise ratio of two. The detection limits are listed in Table 5. The limit of detection for each metal had been corrected for dilution.

Table 5.—Detection limits and limits of detection as obtained by using the described methods.

Metal	Detection limit	Limit of Detection, ppm	
		Water	Sugar
As	0.1 μg	0.003	0.02
Hg	0.01 μg	0.0002	0.003
Cd	0.005 $\mu\text{g}/\text{ml}$		0.001
Cr	0.03 $\mu\text{g}/\text{ml}$		0.006
Cu	0.01 $\mu\text{g}/\text{ml}$		0.002
Fe	0.04 $\mu\text{g}/\text{ml}$		0.008
Pb	0.01 $\mu\text{g}/\text{ml}$		0.002
Mn	0.005 $\mu\text{g}/\text{ml}$		0.001
Zn	0.003 $\mu\text{g}/\text{ml}$		0.0008

Summary

Analytical methods for the analysis of a number of heavy metals, sensitive to submicrogram quantities, in factory water and granulated sugar by atomic absorption spectroscopy have been developed.

The method for determining Cd, Cr, Cu, Fe, Pb, Mn, and Zn is based on concentrating the water by evaporation and sugar by sulfated ashing, with subsequent determination by standard atomic absorption technique.

The determination of mercury involves wet oxidation, reduction of ionic mercury to its atomic state, and followed by flameless atomic absorption measurement of the resulting mercury.

The arsenic determination is based on wet oxidation of the sample, conversion of trivalent arsenic to arsine, and introduction of the arsine into an argon-hydrogen entrained air flame with subsequent quantification by atomic absorption.

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