The Determination of Trace Metals in Process Juices and White Sugar

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Introduction

The analysis for trace metals is rapidly becoming routine in many industries. Metals as well as non-metals have been determined quite accurately for many years, but in most cases have required analytical procedures that are extremely time consuming. Many colorimetric procedures are very accurate when care and good technique are applied. However, there are usually a number of steps where small errors can be made that are multiplied in the final results.

The primary purpose of this paper is to determine "if" and "how" atomic absorption spectrophotometry can be applied to the determination of trace metals in process juices and white sugar. Of equal importance is the evaluation of atomic absorption and its application in providing rapid and accurate analysis for research and industrial problems.

The use of atomic absorption spectrophotometry as an analytical tool is now firmly established. (2, 3, 6)[2] This is apparent from the number of technical papers that have been published during the past few years. The field of analytical chemistry is developing so rapidly that much of the published information is out-dated before it reaches the reader. There has been an increasing interest in the presence of trace amounts of metals in certain products. An analytical report that simply states "trace" or "not detected" in many cases is no longer accepted. With this thought in mind, sugar technologists must explore new, faster, and more sensitive, direct means of determining trace metal content of white sugar and process juices.

Theory

In emission, which is the basis for flame photometry, atoms are excited and raised to a higher energy level. As these atoms return to their ground state they emit energy in the form of light of a specific wavelength characteristic of that element. Therefore, the intensity of this light is proportional to the concentration of the excited atoms.

However, in atomic absorption, as shown in Figure 1, light from a hollow cathode lamp made from the element of interest is passed through the flame and into the spectrophotometer where a resonant wavelength is isolated by the monochromator.

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[2] Numbers in parentheses refer to literature cited.

When a sample is atomized into the flame nearly all of the atoms are in the ground state and are capable of absorbing the resonant wavelength. This absorption is directly proportional to the number of atoms being atomized and can be related to concentration.

The limit of detection is dependent on the intensity of the primary light source, signal to noise ratio, ionization potential and flame temperature. Sensitivities vary with the elements to be determined. For example, magnesium produces a higher intensity light than iron and consequently can be detected at much lower concentrations. Magnesium is detectable down to 5 ppb whereas iron is only detectable to about 200 ppb.

As illustrated in the iron spectrum many lines are produced. It would appear that the line produced at 3720 Angstroms (A) would be the best choice. However, the most sensitive lines are 2483 A and 2488 A. The line at 3720 A is about 10 times less sensitive due to effects of nearby lines of emission. Copper produces a very strong line at 3247 A which allows detection limits as low as .05 ppm (Figure 2).
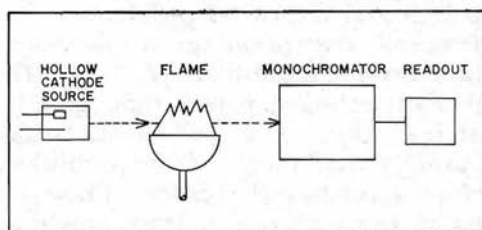

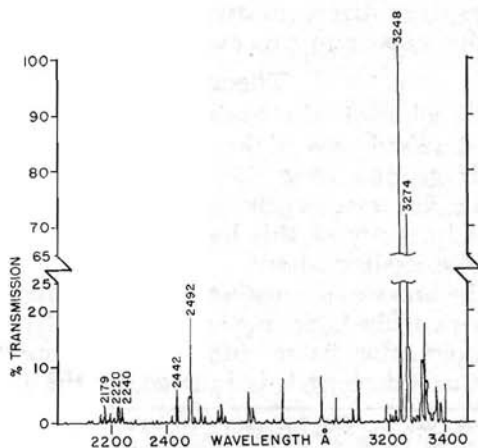Figure 1.—Schematic diagram of atomic absorption single-beam instrument.

Figure 2.—Copper transmission spectrum.

It is now possible to determine virtually all metals by atomic absorption. If a hollow cathode lamp can be manufactured from the metal then this metal can be determined by atomic absorption. If a hollow cathode lamp cannot be manufactured from a particular metal such as phosphorus, then indirect methods may be employed. Non-metals may be determined in certain cases by quantitatively precipitating with a standard metal solution and determining the concentration of the unreacted metal. In these areas of analytical chemistry applications are virtually unlimited with atomic absorption.

Equipment and Procedures

A Beckman Model 979 atomic absorption unit coupled with a 10-inch Sargent Model SRLG linear-log recorder was used for all atomic absorption determinations. The Beckman unit was equipped with an Aztec Model AB-41 total consumption air-acetylene burner head. This burner was selected on the basis of its high dissolved solids handling capacity, ease of cleaning, and variable light path feature. Hollow cathode tubes of the single and multiple element type manufactured by Westinghouse and Aztec were used during this study.

In preparation of samples for analysis for atomic absorption, it was necessary to concentrate certain metals in white sugar. Since the sensitivity of this instrument is only 0.2 ppm on iron and 0.05 ppm on copper it was necessary to remove these two metals from the sugar and concentrate them to the range of the instrument. This was accomplished by passing 300 grams of white sugar in a 30 Brix solution through 15 ml of IRC-120 analytical grade cation resin in the hydrogen form. Water used to take the sugar in solution was decationized and blanks were run along with the samples. The cations removed from the sugar were then removed from the resin with two 25 ml aliquots of hot 3N analytical grade hydrochloric acid and rinsed with 50 ml of hot decationized water. The solution was evaporated to dryness and taken up in 10 ml of 5% HCl solution. This solution was analyzed for iron, copper, magnesium, calcium, sodium and potassium.

Magnesium and calcium have much lower detection limits, so it was possible to determine these two elements on dilute solutions of white sugar. Dilutions necessary to avoid viscosity and interference problems were 15g of white sugar diluted to 100 ml with decationized water containing 0.1% lanthanum. To avoid interference problems in process juices it was necessary to dilute raw juice, thin juice, thick juice and molasses to approximately 5 Brix. Recovery studies were made on all samples by the method of standard additions. Analyses were also carried out on ashed samples for comparison.

Figure 3 gives the flame characteristics and instrument settings for each element. Once these settings have been established the standard curve can be reproduced very quickly. Fuel and support mixture is important as well as slit width and lamp current. Each of these settings is established for best operating parameters.

Figure 4 illustrates recovery of iron from white sugar by the ion exchange methods. This sample was duplicated and 100% recovery was obtained.

	IRON	COPPER	CALCIUM	MAGNESIUM	ALUMINUM	SILICON
WAVELENGTH	2483Å 2488Å 3720Å	3248Å 3274Å	4227Å 2398Å	2853Å 2026Å 2796Å	3092Å 3093Å 3962Å	2516Å
SLIT	0.25mm	0.05mm	0.10mm	0.10mm		
FUEL	ACETYLENE 5 psig	ACETYLENE 5 psig	ACETYLENE 7 psig	ACETYLENE 7 psig	ACETYLENE	ACETYLENE
SUPPORT	AIR 14 psig	AIR 15 psig	AIR 12 psig	AIR 15 psig	NITROUS OXIDE	NITROUS OXIDE
LAMP CURRENT	12 mA	10 mA	15 mA	30 mA		
FLAME	OXIDIZING NON LUMINOUS	OXIDIZING NON-LUMINOUS	REDUCING FUEL RICH LUMINOUS	REDUCING FUEL RICH LUMINOUS		

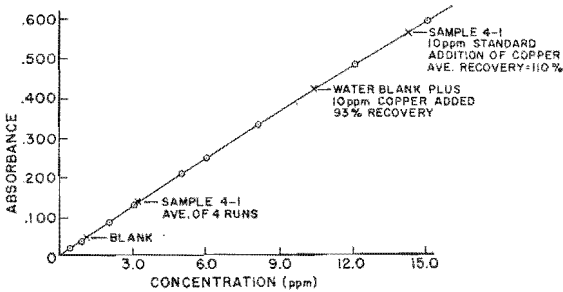Figure 3.—Flame characteristics and instrument settings.

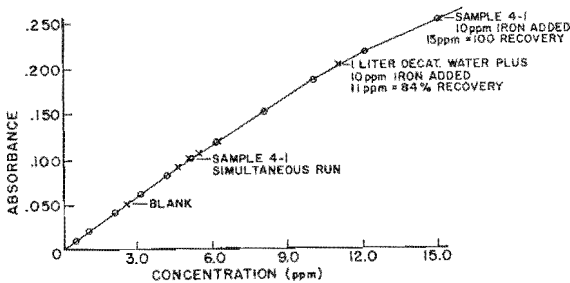Figure 4.—Iron recovery from white sugar using IRC-120 analytical grade cation resin.

Figure 5.—Copper recovery from white sugar using IRC-120 analytical grade resin.

In Figure 5, on an average of four runs, copper recovery amounted to an average of 110%. Only one blank was run which gave 93% recovery. Differences in samples might possibly account for the high recovery figure.

Experimental Results

The first action was the determination of calcium, magnesium, iron, copper, sodium and potassium in process juices. Some interferences were encountered in the determination of magnesium and calcium but were eliminated with the addition of lanthanum.

Interferences in the determination of calcium and magnesium have been thoroughly explored (3, 6). Phosphates, sulfates, silica and aluminum are known interfering elements. The addition of lanthanum eliminates virtually all of the known interferences by tying up these compounds and allowing the calcium and magnesium to be completely atomized in the flame. No interferences have been reported in the determination of iron and copper (3). Figure 6 shows copper recovery in molasses. Dilutions of 1:20 were necessary to obtain 100% recovery.

Average metal concentrations in process juices are listed in Table 1. Since potassium is consistent throughout the processing cycle, results are calculated as percent on potassium. Results indicate possible elimination and corrosion patterns throughout the factory process. If these results are consistent, in future studies it may be possible to pinpoint corrosion problems or other trouble areas. Results show that these metals are present and can be traced throughout the factory. Analyses of ashed samples were consistent with analysis on straight process juices indicating that process juices can be analyzed directly with accurate results.
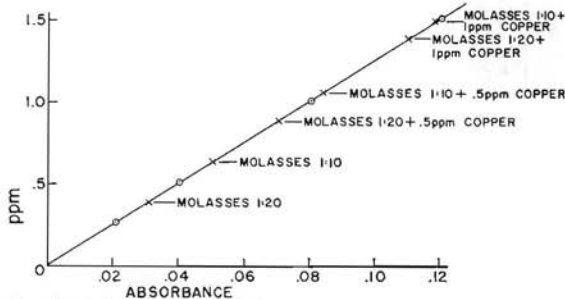

Figure 6.—Copper recovery in molasses.

Table 1.—Trace metals in process juices.

	Brix	Mg. sug./ml.	Conc. units	Na	K	Mg	Mg ashed	Ca	Ca ashed	Fe	Fe ashed	Cu
Diffusion Supply Water			P.P.M.	78	162	20.5	12.1	37.0	13.0	16.0	13.3	.019
			% on potassium			12.7		22.8		9.88		.17
Raw juice	15.3	134.6	P.P.M.	610	1740	355	306	79.0	80	22.6	40.5	0.11
			% on potassium			20.4		4.5		1.3		.0063
Thin juice	15.0	139.8	P.P.M.	580	1910	6.5	6.0	65.8	62.5	2.2	2.2	.015
			% on potassium			3.4		6.0		0.12		.0079
Thick juice	66.8	798.5	P.P.M.	2040	6400	38.8	40.0	328	272	19.5	50.0	0.6
			% on potassium			6.1		5.1		0.3		.022
Molasses	87.75	812.2	P.P.M.	13600	28500	214	204	1330	1264	100	212	4.1
			% on potassium			7.5		4.7		0.35		.027

Copper seemed to be one exception, but results from ashed samples were disregarded when it was established that the hydrochloric acid used to dissolve the ash contained copper impurities and the acid was possibly enhancing the copper absorption signal.

Figure 7 shows the calibration curve when determining magnesium in low concentration in diluted white sugar samples. It also shows the detection limits based on 1% (.005) absorption which is equivalent to .005 ppm (5). This is an extremely low concentration but quite reproducible when maintaining noise and interference at a minimum. Figure 8 illustrates the calibration curve for magnesium and its detection limits in single pass-normal burner position. This does not mean that magnesium and calcium can only be determined in these low concentrations. Actually, by turning the burner head for minimum light passage through the flame it is possible to read up to 20 ppm magnesium and 50 ppm calcium. This means that the range is at least 1000 fold on these two elements. However, the range is only approximately 20 fold in the case of iron.
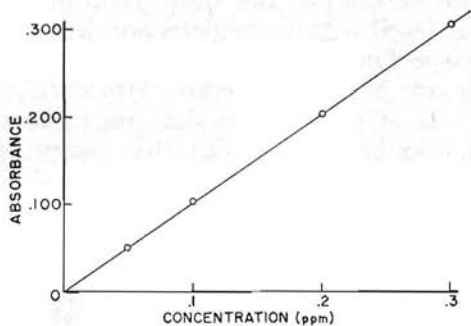
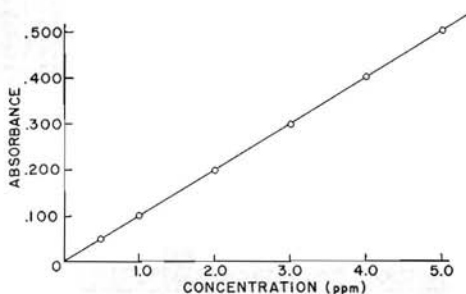Figure 7.—Calibration curve for magnesium using triple pass.

Figure 8.—Calibration curve for magnesium using single pass-normal burner position.

Table 2.—Magnesium and calcium in white sugar (15g diluted to 100 ml).

| | Calcium | | | | | | Magnesium | | | | |
| | Absorbance | | ppm | | | | Absorbance | | ppm | | |
Sample	1	2	1	2	Avg	Avg*	1	2	1	2	Avg
1-A	.02	.027	2.27	2.20	2.24	1.95	.013	.013	.07	.07	.07
1-B	.086	.086	7.07	7.07	7.07	8.45	.048	.044	.33	.31	.32
2-A	.017	.017	2.10	2.10	2.10	2.40	.015	.016	.09	.10	.10
2-B	.060	.060	4.93	4.93	4.93	5.55	.018	.017	.11	.11	.11
3-A	.023	.021	1.87	1.83	1.85	----	.025	.020	.16	.13	.15
3-B	.014	.014	1.20	1.20	1.20	----	.034	.030	.23	.20	.22
4	.126	.024	10.40	2.00	----	---- **	.037	.250	.25	1.67	---- **
5	.057	.058	4.80	4.80	4.80	----	.009	.010	.05	.05	.05
6	.040	.039	3.33	3.33	3.33	----	.120	.119	.87	.87	.87
7	.026	.024	2.13	2.00	2.07	----	.015	.015	:09	.09	.09

* Average from ashed sample.

Table 2 lists results obtained by directly aspirating unfiltered samples of white sugar (15 grams diluted to 100 ml with de-cationed water). These white sugar samples represent high and low color and turbidity samples from four different sugar companies. Absorbance is quite low on high quality white sugar. Note that duplicate samples are quite reproducible and absorbance readings are well within the detection limits. Some readings are just above the lowest detection limit, but concentrations of this magnitude are of little concern. However, readings in the order of 0.126, as in the high oxalate sugar, may be quite significant. It should be pointed out that sampling is important
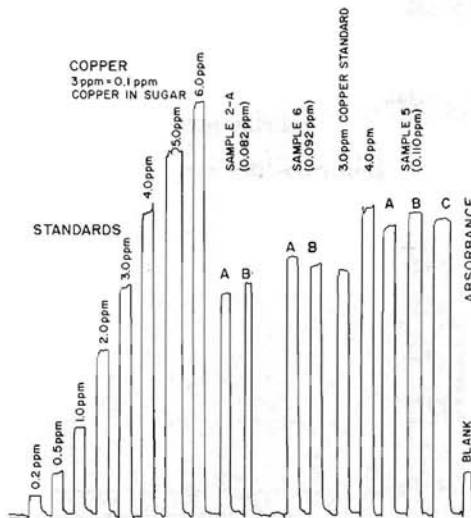

Figure 9.—Copper determinations on 10 milliliter samples concentrated from 300g of white sugar.

as is demonstrated by the range of results on sample 4 which is a high oxalate sugar. This indicates a non-homogeneous mixture and the presence of these elements in random particulate matter.

In Figure 9 the resulting data for copper are shown for several determinations on the 10 milliliters concentrated from 300g of white sugar through the ion exchange resin.

Table 3 gives complete analyses of all samples. Magnesium ranges from .05 ppm in high quality sugar to 1.67 ppm in low quality sugar. Calcium ranges from 1.20 ppm to 10.4 ppm. Copper ranges from .07 ppm to .230 ppm and iron from .058 ppm to .273 ppm.

Sodium and potassium also show a wide range. In sample series 1 through 3 (A) and (B) sugar samples are high and low quality sugars respectively.

Table 3.—Trace metals in white sugar—averages from Table 2 and 4.

Sample	Ca (ppm)	Mg (ppm)	Cu (ppm)	Fe (ppm)	Na (ppm)	K (ppm)
1-A	2.24	0.07	.077	.058	8.13	5.99
1-B	7.07	0.33	.126	.193	8.00	6.66
2-A	2.10	0.10	.082	.104	8.53	7.32
2-B	4.93	0.11	.230	.138	16.0	22.98
3-A	1.80	0.15	.023	.148	10.53	14.82
3-B	1.20	0.20	.062	.190	17.86	28.64
4	2.00 to 10.40	0.25 to 1.67	.119	.200	9.73 to 24.92	—
5	4.80	0.05	.110	.205	4.80	1.33
6	3.33	0.67	.092	.273	2.92	1.66
7	2.00	0.09	.138	.158	4.13	—

Table 4.—Copper and iron determination in white sugar.

Sample	Iron			Copper		
	Run A	Run B	Average	Run A	Run B	Average
1-A	.057		.058	.072	.083	.077
1-B	.193	.193	.193	.113	.145	.126
2-A	.113	.095	.104	.083	.081	.082
2-B	.138	.138	.138	.230	.230	.230
3-A	.138	.158	.148	.023	.023	.023
3-B	.213	.178	.190	.060	.064	.062
4	.180	.220	.200	.117	.121	.119
5	.221	.190	.205	.107	.113	.110
6	.283	.263	.273	.093	.090	.092
7	.158		.158	.138		.138

Summary

Experimental data were presented which indicates the utility of atomic absorption techniques in determining trace metal concentrations in white sugar, process juices and liquors.

With certain refinements the atomic absorption methods presented should attain an accuracy and precision equal to or surpassing classic trace metal extraction methods. The advantage of the direct method of analysis in time saved is apparent. Extension of direct trace metal determinations to zinc, aluminum and silica in white sugar, process juices and liquors should not pose any significant problem.

Literature Cited

(1) AMOS, M. D. 1966. The Element Technical News Notes from Aztec Instruments, Inc. (7). Westport, Conn.

(2) BELCHER. R., and C. L. WILSON. 1964. New Methods of Analytical Chemistry. Chapman and Hall Ltd. London. 366 p.

(3) ELWELL, W. T., and J. A. F. GIDLEY. 1966. Atomic Absorption Spectrophotometry, Pergamon Press. New York. 139 p.

(4) MORRISON, G. H., and H. FREISER. 1957. Solvent Extraction in Analytical Chemistry, John Wiley and Sons, Inc. New York. 269 p.

(5) MUNOS, R. J. 1967. Beckman Flame Notes 11 (1). Fullerton, Calif.

(6) ROBINSON, J. W. 1966. Atomic Absorption Spectroscopy, Marcel Dekker, Inc. New York. 204 p.