

Trace Mineral Salt Analysis with Atomic Absorption Spectrophotometry

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ABSTRACT

A Trace Mineral Salt is a mixture of salt and trace minerals in a ratio of about 98:2. Salt, in addition to its nutritional value, is used as a carrier for trace minerals.

Prior to use of atomic absorption as an analytical means, quality control of the finished trace mineral salt product was mainly dependent on inventory control. Conventional analytical means for many trace minerals are so cumbersome and lengthy that the analyses were: "after-the-fact," and of only historical value.

Atomic absorption spectroscopy is the study of absorption of radiant energy by atoms. As an analytical process it includes the conversion of combined elements to atoms and the absorption of radiant energy by those atoms. The major application of atomic absorption spectroscopy is the detection of trace metal constituents. Advantages of this means are: high sensitivity, relatively free of interference, and rapid and minimal amount of pre-treatment.

The basic instrument consists of a light source, a burner-atomizer, a monochromator, a sensing device, usually a photomultiplier, and means to provide an output.

After considerable development, atomic absorption spectroscopy has provided a means for overcoming many limitations encountered with conventional procedures. Although it has been successfully adapted to several elements, some require further investigation.

Still others, although generally applicable, are unsuccessful for unknown reasons.

INTRODUCTION

A Trace Mineral Salt is a Trace Mineral actually mixed with salt in such a manner as to ideally produce a non-segregating, heterogeneous mix of salt and a trace mineral essential to animal nutrition. Salt, in addition to its nutritional value, is a carrier for trace minerals. These are mixed in a ratio of about 98% salt to 2% of trace minerals. The elemental analysis of a Trace Mineral Salt composition could be:

Iodine .02%	Copper .02%	Manganese .500%
Iron .01%	Cobalt .005%	Zinc .25%

This is only an example and could vary considerably, dependent on the use of the product.

In application at the Hardy Salt Company Plant in Manistee, Michigan, the product is mixed at a rate of 1500-2000 lbs/min. Some of the Trace Minerals, present in very small amounts, are premixed and others such as the Iodine source are treated with a stabilizer and premixed with salt. Due to the nature of the process, in an ideal quality control program, it is essential to:

1. Analyze the incoming chemicals
2. Analyze the premixes prior to using
3. Analyze the product prior to packaging
4. Analyze the finished product according to a statistical sampling plan

A rapid analytical means for the quantitative measurement of trace minerals is essential in order to accomplish these analyses. Without such a means the quality control program is dependent mainly on inventory control.

PREVIOUS ANALYTICAL PRACTICE

Conventional analytical procedures for many trace minerals are so cumbersome and lengthy that the analyses are "after-the-fact" and of only historical value. As an example, the previously used conventional analytical method for Zinc requires approximately 6 man hours and an elapsed time of 32 hours. Upon completion its accuracy is less than $\pm 5\%$.

In addition to the conventional analytical means including gravimetric analysis, volumetric analysis and colorimetric analysis, the Hardy Laboratory has investigated other methods which might be applicable. A method to be practical for application under conditions of production described ideally should have the following attributes:

1. Relatively inexpensive
2. Rapid (requiring minimal amount of pretreatment)
3. High sensitivity
4. Relatively free of interference
5. Simple—completed by comparably unskilled technician
6. Results independent of human error

As anyone familiar with quantitative chemical analysis is aware, the conventional methods for analysis of trace minerals do not meet all the above requirements.

Some of the more unconventional methods the Hardy Laboratory has investigated are:

1. Flame Photometry
2. Dropping Mercury Electrode
3. Spectrographic analysis

Each of these methods was rejected for failure to meet one or more of the required attributes.

Spectrographic analysis requires expensive equipment and skilled technicians. Flame photometry requires pretreatment to eliminate Sodium, as the presence of comparatively large quantities of Sodium causes interference.

INVESTIGATION OF ATOMIC ABSORPTION SPECTROPHOTOMETRY

In the last few years Atomic Absorption Spectroscopy was developed to the point where equipment was available from laboratory supply sources. The cost of the equipment was such that it appeared feasible to investigate the use of this tool. As an analytical process Atomic Absorption Spectroscopy is based on the absorption of radiant energy by atoms. It includes the conversion of the combined element to atoms and the absorption of

radiant energy by those atoms. The major application of Atomic Absorption Spectroscopy is in the quantitative detection of trace mineral constituents. Advantages of this means of analysis as stated in literature are:

1. High sensitivity
2. Accuracy and precision
3. Relatively free of interference
4. Minimal amount of pretreatment
5. Simple to operate with results independent of human error

As shown in Figure 1 the procedure is highly sensitive and applicable to many elements. Most of the elements can be detected at the ppm level or less.

High precision and accuracy are obtainable by use of calibration curves. Because the absorption signal is practically free of interference, it is a simple matter to make calibration curves and it is not normally necessary to compensate for possible interfering compounds. Metals absorb at well-defined wave lengths and over narrow band widths; thus, absorption interference by atoms of other elements is rare.

The equipment is comparatively simple to operate. Unskilled technicians after minimal amounts of training can run routine analyses.

The instrument is comparatively inexpensive in comparison to many other methods. Total cost of equipment as shown in Figure 2 is about \$4,000.

A schematic diagram of the basic instrument is shown in Figure 3.

As noted it is comparable to other spectroscopic instruments in that it consists of a radiant energy source, a flame atomizer, a monochromator and a registering meter. The source of radiant energy is normally a hollow cathode tube. The tube is composed of the same element as that under analysis and emits a spectrum characteristic of that element.

In operation the hollow cathode tube emits a radiant energy signal I_0 , as shown in Figure 4.

This is usually an electronically modulated tube, and thus the output is an AC signal. The flame into which the sample solution is atomized emits a radiation signal and absorbs signal I_1 as illustrated in Figure 4.

The ground state metal atoms absorb the signal I_1 . Thus after passing thru the atomizer the signal is $I_0 - I_1 \rightarrow I_{2c}$ plus Sdc. The monochromator passes only the wave length detected, and the detector (photomultiplier tube) is tuned to the same signal frequency and synchronized. Thus it is

<u>Element</u>	<u>Resonance Line</u>	<u>Sensitivity ppm</u>	<u>Analytical Range ppm</u>
Aluminum	3092 A	0.8	20-200
Antimony	2176	0.1	10-100
Arsenic	1937	1.0	20-200
Barium	5536	3.5	20-200
Bismuth	2231	0.1	10-100
Boron	2497	250	No Data
Cadmium	2288	0.004	0.5-5.0
Calcium	4227	0.08	2-20
Cesium	8521	0.15	No Data
Chromium	3577	0.006	2-20
Cobalt	2407	0.013	4-40
Copper	3247	0.005	2-20
Gold	2428	0.01	2-20
Iron	2483	0.1	2-20
Lead	2170	0.013	4-40
Lithium	6708	0.03	1-10
Magnesium	2852	0.001	0.2-2.0
Manganese	2795	0.005	2-20
Mercury	2587	0.5	20-200
Molybdenum	3133	0.5	1-100
Nickel	2320	0.01	2-20
Platinum	2659	0.7	10-100
Rhenium	3460	0.3	No Data
Selenium	1960	0.5	10-100
Silicon	2516	0.15	No Data
Silver	3281	0.05	2-20
Sodium	5890	0.03	5-10
Strontium	4607	0.05	2-20
Tin	2863	0.025	25-200
Vanadium	3184	7.0	No Data
Zinc	2139	0.0005	0.5-5.0

Figure 1. Resonance line and sensitivity limits of elements for which hollow cathode tubes are commercially available.

PURCHASE LIST

Atomic Absorption Spectrophotometer—Model 140		\$2850.00
Hollow Cathode Tubes		
Cobalt		90.00
Copper		90.00
Iron		90.00
Manganese		95.00
Zinc		90.00
Calcium—Magnesium—Aluminum		120.00
Atomic Absorption Standard Solutions		
Calcium	1,000 ppm	5.00
Calcium	10,000 ppm	5.00
Copper	1,000 ppm	5.00
Cobalt	1,000 ppm	5.00
Iron	1,000 ppm	5.00
Manganese	1,000 ppm	5.00
Magnesium	1,000 ppm	5.00
Zinc	1,000 ppm	5.00
Gas pressure regulator for acetylene		40.00
Air Regulator and Dehydration Chamber		80.00
Beakers	1 dozen	8.00
Plastic Elbows	1 dozen	2.50
Capillaries	package of 6	9.25
Acetylene—continuing use	tank	6.00
Lanthanum Chloride—continuing use	1 lb.	40.00
Silica Gel—spare for dehydration chamber	5 lb.	9.45

Figure 2. Price of atomic absorption spectrophotometer and auxiliary equipment.

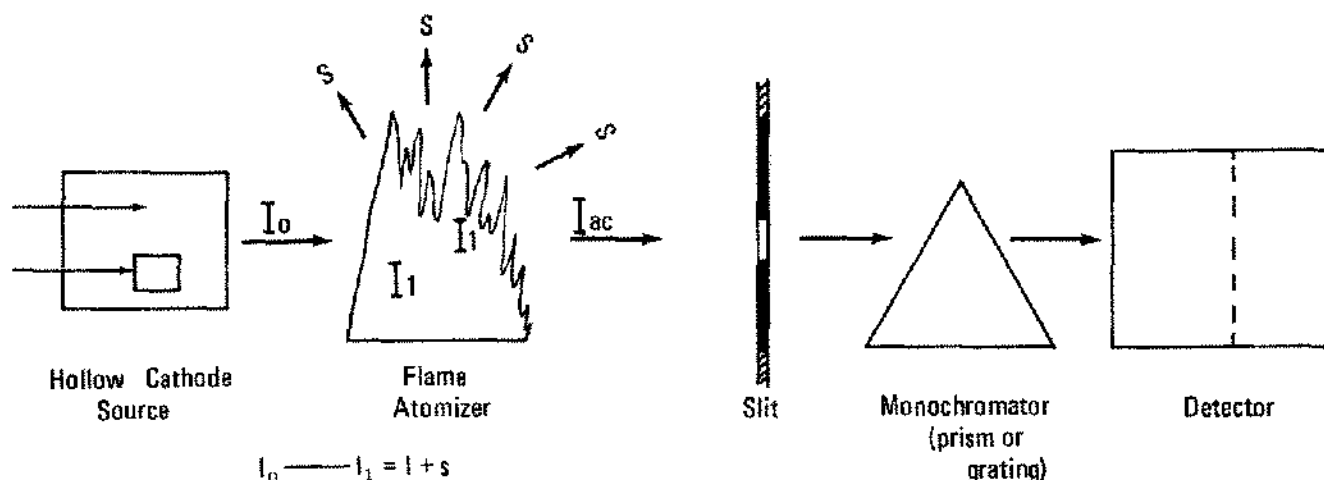


Figure 3. Schematic diagram of basic atomic absorption instrument.

sensitive to the AC signal only and reads I_{ac} which is the difference between the energy emitted by the hollow cathode tube and the amount of energy absorbed by the light absorbing atoms in the material being analyzed. There are many more ground state light absorbing atoms in a metal than atoms in the light emitting energized state. This fact accounts for the much greater sensitivity of this method compared to emission spectroscopy. The instrument meter reads the % absorption directly. In actual operation the instrument is first zeroed by using a blank (distilled water). This would show maximum intensity (no absorption). It is also checked for infinity on the meter by cutting off the light source (100% absorption).

ADAPTION AT HARDY LABORATORY

The Hardy Laboratory was interested in analyzing for the metals shown in Figure 5.

In addition this figure shows the type of cathode, the wave length used, and the extent to which they have presently developed methods.

The laboratory initially ran into difficulties in applying the Atomic Absorption Spectrophotometer. Approximately 6 months elapsed between the time of initial delivery of the instrument and its routine use for analysis. On initial trials with the instrument duplicate results or normal absorbance levels with the standards could not be obtained. Comparison of initial results with the normal is shown in Figure 6.

The laboratory in cooperation with the suppliers' technical service representative went thru the following steps prior to the routine use of the instrument. In an attempt to overcome this unsatisfactory operation the atomizer was checked to assure it was not partially blocked. Next the photomultiplier tube was replaced. These efforts did not correct the situation and after again contacting the supplier they advised that there must be a malfunction in the electronic system. They advised returning the instrument to their laboratory for checking. While the instrument was at their laboratory, they reportedly replaced the mixing chamber and checked out the electronics. On return of the instrument to The Hardy Salt Company Laboratory, the same problems were still encountered. The suppliers' technical representative then came to the plant and realigned the cathode tube, burner, and slit. He also calibrated the wave length selector to correspond to the new photomultiplier tube. At this time he stated that the latter is necessary whenever a new tube is installed.

At this point the laboratory was able to set up standards and develop reliable procedures for Calcium, Manganese, Copper, and Iron. Reliable results could not be obtained for Zinc or Cobalt. The instrument supplier provided a new Cobalt tube and a new Zinc cathode tube. On using the new Zinc tubes Zinc could be analyzed with good results.

Problems are still encountered in Cobalt analysis. The standard curve can be obtained, using

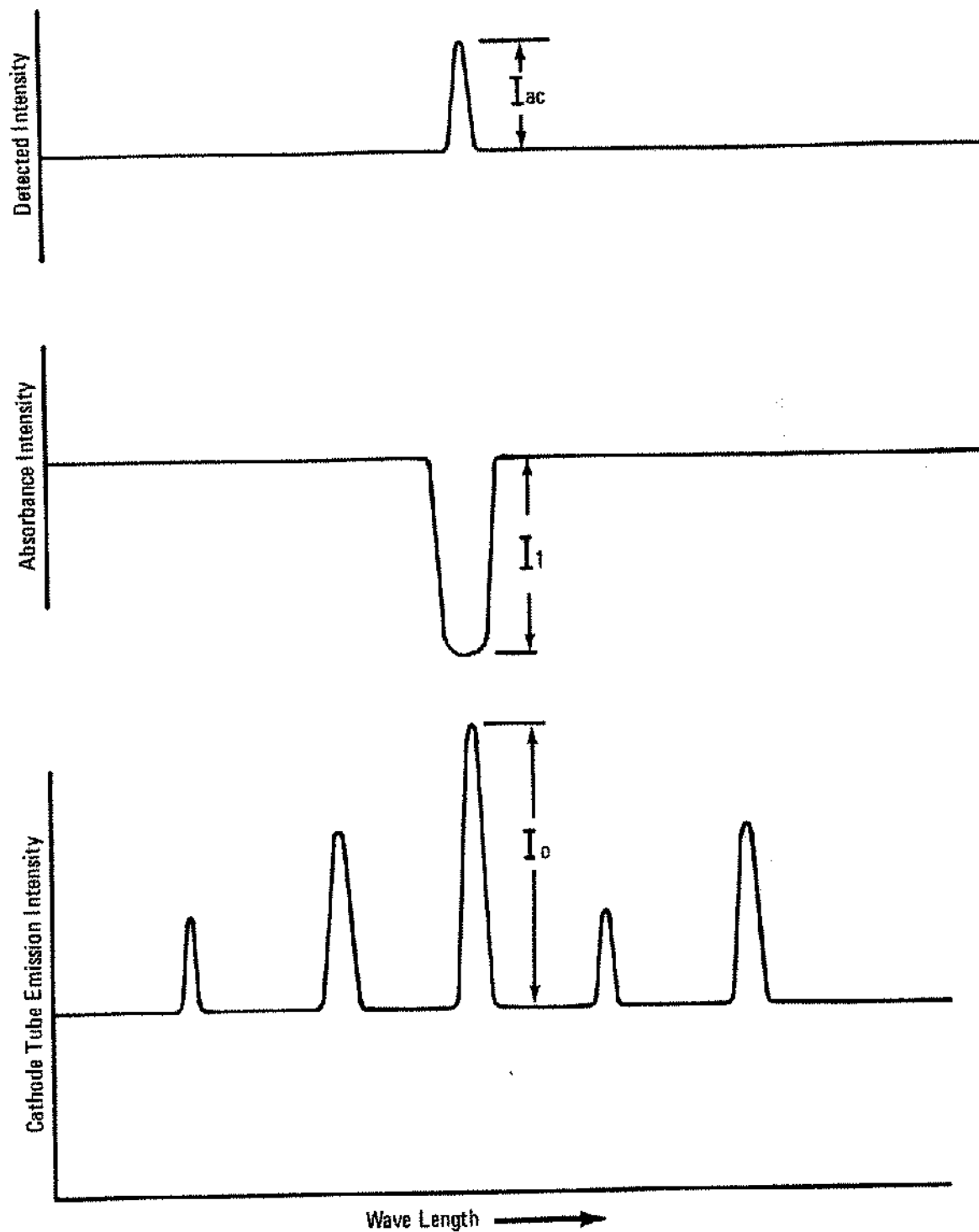


Figure 4. Radiation lines emitted by cathode tube, absorbance by flame and difference by modulator and detector.

Element & Cathode	Wave Length A°	Used routinely	Available not used routinely	Tried-no successful method to date	Not available could have future application
Manganese	2795	X			
Copper	3247	X			
Zinc	2139	X			
Iron	2483	X			
Cobalt	2407			X	
Calcium *	4227	X			
Magnesium *	2852		X		
Aluminum *	3092		X		
Lead	2170				X
Barium	5536				X
Arsenic	1937				X
Nickle	2320				X
Lithium	6708				X
Potassium	7665				X

* Note: Calcium-Magnesium-Aluminum is a multi-element tube

Figure 5. Metals requiring analysis by Hardy Laboratory and extent of use at present.

standard Cobalt solutions, but the results on production samples are always either very high or very low compared to theoretical levels or values obtained by past methods. Further, the results are not reproducible. It is presently believed the low level of Cobalt in comparison to the high salt level in the sample, which makes marked sample dilution impractical, is the cause of the low results. The high salt content of the sample causes blockage of the capillary tube to the burner atomizer and prevents sample pick-up, thus low results. The high results are possibly due to Calcium interference. Calcium, in addition to its major wave length of absorption, has a secondary wave length of 2399Å which is very close to the detecting wave length of Cobalt 2407Å. Upon the recommendation of the supplier, both a lanthanum solution was tried, and an ultra fine filter (a Gelman membrane capsule filter mean pore size .45M) was tried to eliminate the interference. Neither of these methods were successful.

Other possible means that have not been tried are:

1. Chelating agents to tie up the Calcium
2. Enrichment of the solution with a known Cobalt concentration

These and other possible means are being investigated in order to develop a workable method.

A typical procedure (Manganese) as developed by the Hardy Laboratory is shown in Figure 6.

On perusal of this table it is readily noted that the method is shorter and requires less chemical "know-how" than the normal colorimetric, volumetric, or gravimetric methods for determining Manganese.

On comparing results obtained by previous methods used by Hardy Laboratory with the Atomic Absorption Spectrophotometric method as presently developed, there are the following advantages of the latter method.

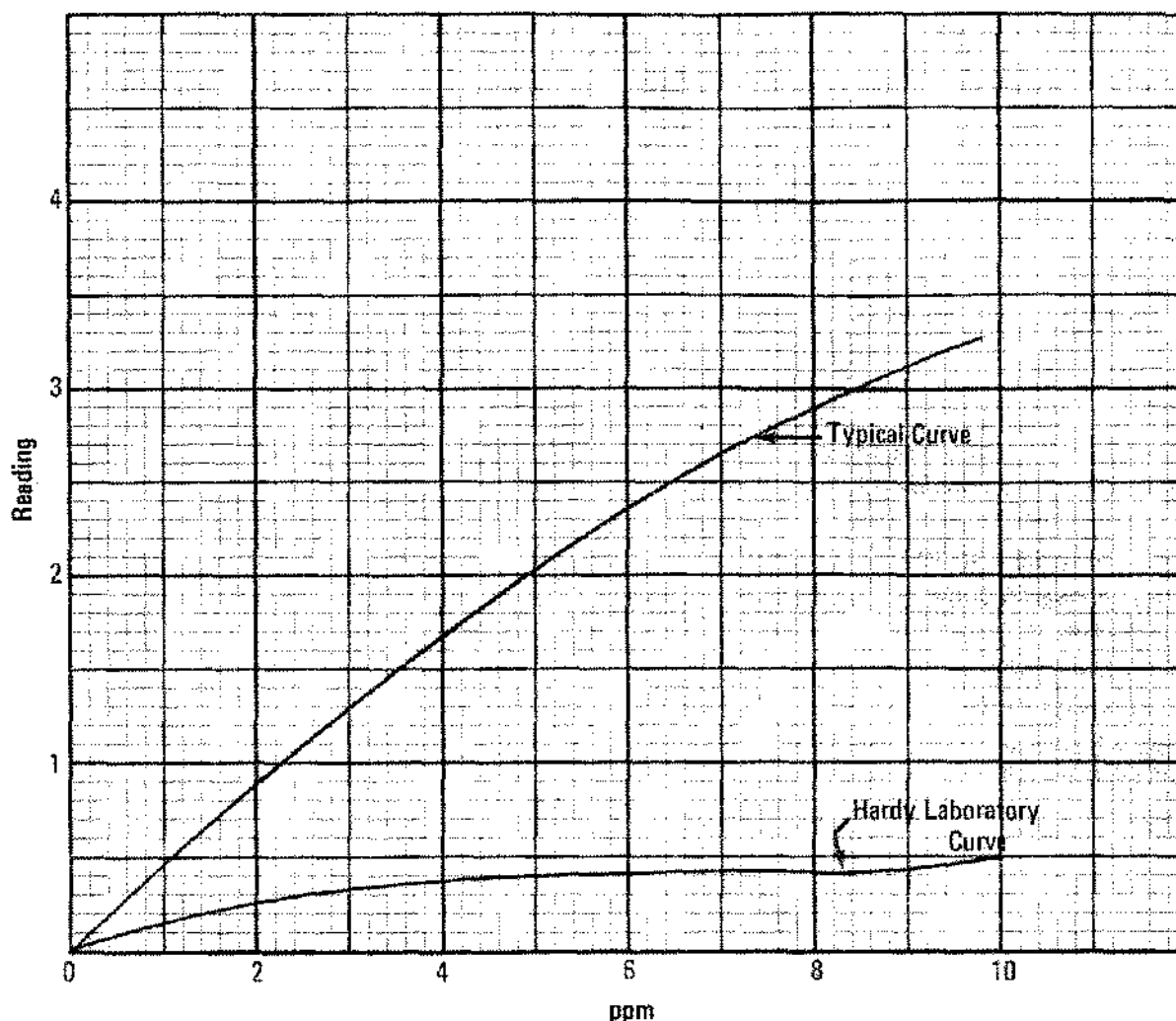


Figure 6. Manganese Typical calibration curve vs. Initial Hardy Salt Co. laboratory curve.

the analysis of Manganese, Copper and Iron a gravimetric method using the Spectronic 20 as a measuring means was previously used. In each case it was necessary to dissolve the sample with a mineral acid, filter the dissolved sample, dilute to suitable concentration, remove the interfering ions by addition of chemical to form a ppt or by the element being tested and filtering. The procedure was then developed by various means. At this time the concentration of the trace mineral was determined by means of the Spectronic 20.

The time consuming and technical portion of the procedure is the removal of the interfering ions and development of the color. Both of these steps have been eliminated in the Atomic Absorption procedure.

In determination of Calcium the gravimetric procedure, whereby the Calcium is precipitated and determined as Calcium Oxalate was used. A gravimetric procedure requires a skilled technician to obtain reliable results. The procedure is also tedious and time consuming.

The previously used procedure for Zinc was unreliable in addition to being very lengthy and requiring skilled personnel. The results were of such questionable value in comparison to known inventory additions that quality control was based on inventory of additions.

All minerals that are presently analyzed for by the Atomic Absorption Spectrophotometric method can be completed in approximately ½

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Determination of Manganese by Atomic Absorption Spectrophotometer

Application:

Incoming raw materials containing Manganese
Trace Mineral Salts

Reagents:

20 ppm standard Mn solution
Conc. Sulfuric Acid.

Procedure:

1. Reduce sample to 50 gm by using the riffle sampler.
2. Place sample into a 500 ml volumetric flask and add 400 ml of water.
3. Add 10 ml of conc. H_2SO_4 .
4. Place on magnetic stirrer and stir until dissolved. Let stand overnight.
5. Dilute to mark and mix.
6. Filter through Muntells # OK filter.
7. Place a 5 ml aliquot into a 1000 ml volumetric flask and dilute to mark with distilled water.
8. Place Mn tube in AAS and turn on $\frac{1}{2}$ hr. prior to using.
9. Set machine as follows:

wavelength	280 mu	(2795 A°)
slit width	.05 mm	
gas press	8 lb/in ²	
air press	12 lb/in ²	
lamp range	3	
10. Obtain a zero scale reading while aspirating distilled water.
11. Aspirate 20 ppm standard solution, rotate the burner until a reading of 60 is obtained.
12. Aspirate the sample and obtain reading—determine ppm Mn from chart.

Calculations:

ppm Mn from chart $\times 0.2 = \% \text{ Mn in original sample.}$

Figure 7. Procedure for determining Manganese by atomic absorption spectrophotometer.

hour. This is a considerable time saver over the 2 to 6 hours required by previous methods.

As shown in Figure 8 there is a savings in time and an increase in accuracy when using the Atomic

Absorption Spectrophotometric method of analysis.

In each case the Atomic Absorption Spectrophotometric method is much shorter and in most applications is more accurate than the previous method. The accuracy of the Atomic Absorption Spectrophotometric method in comparison to the conventional method is still greater when one considers the human errors possible.

CONCLUSIONS

The instrument supplied to the laboratory posed several problems prior to its successful adaptations for routine use. The initial problems appeared due to either a faulty instrument or poor initial adjustment by suppliers technicians. While it has not been the ideal answer to all requirements it has provided a means for determining Copper, Iron, Manganese, Zinc and Calcium with the following advantages:

1. Marked savings in man hours required per analysis
2. Analyses of equal or better precision than achieved with previous methods
3. Greater reproducibility of results with unskilled technicians
4. Savings in equipment replacement and chemicals
5. Provides a potential means for the simple determination of other elements in contrast to other standard procedures for which our laboratory does not have the necessary equipment or chemicals to practice the procedure.

ACKNOWLEDGEMENT

The writer wished to acknowledge that the developmental work on the application of the Atomic Absorption Spectrophotometer as an analytical tool for the analysis of Trace Mineral Salt was done by Robert Topel, Plant Chemist, Hardy Salt Company.

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ELEMENT	ATOMIC ABSORPTION			CONVENTIONAL		
	Man hours	Elapsed Time-hours	Accuracy	Man hours	Elapsed Time-hrs.	Accuracy
Manganese—MnO	.7	18	+2%	2	22	+2%
Manganese—Mn SO ₄	.7	2½	+2%	2	18	+2%
Copper	.7	2½	+2%	1.5	3.5	+4%
Iron	.7	2½	+2%	2	4	+5%
Zinc	.7	2½	+2%	6	32	?
Cobalt	.7	2½	*	5	20	+2%
Calcium—EDTA	.7	2½	+2%	.2	.2	+4%
Calcium—gravimetric				4	6-10	+6%
Magnesium—EDTA	.7	2½	+2%	.2	.2	+6%
Magnesium—gravimetric				4	6	+6%

*No reliable method developed.

Figure 8. Time and accuracy comparison of atomic absorption spectrophotometric method and conventional methods used by Hardy Laboratory for analysis of trace minerals.

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