1963

A Simple Atomic Absorption Photometer for Water Analysis.

Charles Bernard Herrin
Louisiana State University and Agricultural & Mechanical College

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FOR WATER ANALYSIS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Charles Bernard Herrin
B.S., University of Oklahoma, 1958
M.S., University of Oklahoma, 1960
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ABSTRACT

The design and construction of a simple atomic absorption photometer using light filters is described. Most of the components are readily obtainable by most laboratories, and no special skills are required for the construction. The instrument is intended for the determination of sodium, potassium, calcium, and magnesium in natural waters.

The basis for the determinations is the attenuation of a beam of monochromatic light by gaseous atoms. Atoms in the ground state will absorb light if the energy of the photons is equal to the transition energy from the ground state to the first excited state.

Monochromatic light, generated by the excitation of atoms of the metal to be determined, is passed through a flame into which a solution containing a salt of the metal to be determined is sprayed. The flame decomposes the metal salts and produces gaseous atoms in the ground state. The amount of light absorbed in the flame is proportional to the concentration of the metal salt in the solution.

Methods for overcoming the common interferences apt
to be encountered in natural waters are described. Results of the analyses of natural waters are given, and they are comparable in accuracy and precision with those obtained by conventional methods. When the instrument is in operation, the measurements and calculations necessary to make a determination require about two minutes.
CHAPTER I

INTRODUCTION

Tremendous quantities of water are used each day for industry, agriculture, and human consumption. Therefore, accurate and timely determinations of the mineral content of water are of great economic importance. The conventional methods for performing these analyses are, for the most part, tedious and time consuming. With most of these methods a high degree of proficiency on the part of the analyst is prerequisite for reliable results. Therefore, a method which will give rapid and reliable results in the hands of non-specialized personnel is a very desirable goal.

The four major cations that are routinely determined in the mineral analysis of water are sodium, potassium, calcium, and magnesium.

Sodium generally occurs in higher concentrations in natural waters than the other three. Sodium salts are quite soluble, and when these salts are leached from rocks and soil, they tend to remain in solution. Sodium is not particularly
significant from a physiological viewpoint in the concentration range normally encountered in potable waters, except for persons having an abnormal sodium metabolism. Waters containing a high ratio of sodium to calcium plus magnesium may damage soil if they are used for irrigation. Sodium tends to disperse soil colloids which causes loss of soil permeability (22).

Potassium is almost as abundant in the earth's crust as sodium, but the potassium concentration in natural waters is usually lower. The potassium occurs in rocks in a form that is not easily dissolved. Most natural waters contain less than 20 parts per million of potassium. However, waters containing several hundred parts per million are not rare (22).

Knowledge of the calcium content is of great importance because calcium salts impart hardness to water. In the presence of sulfate or alkaline substances, calcium may cause boiler scale. Small amounts of calcium carbonate are desirable for water used for household purposes because it forms a protective coating in the pipes. A high ratio of calcium to sodium is desired in irrigation water because it flocculates soil colloids and tends to maintain good soil permeability.
Calcium is both abundant and widely distributed in rocks and soil. Furthermore, calcium is dissolved from practically all rocks. The solubility of calcium in different rock forms varies considerably. Waters associated with granite and silicious sand may contain less than ten parts per million of calcium, whereas waters associated with limestone formations generally contain 30 to 100 parts per million of calcium. Concentrations of calcium as high as several hundred parts per million are found in waters which percolate through gypsiferous shale (22). These waters are colloquially called "gyp" waters.

Magnesium is about half as abundant in the earth's crust as calcium. Waters associated with granite and silicious sand may contain less than five parts per million of magnesium. Water from dolomite or limestone rich in magnesium may contain 10 to 50 parts per million. Magnesium sulfate and magnesium chloride are quite soluble, and water in contact with these salts may contain several hundred parts per million (22).

Magnesium salts are one cause of water hardness, and, therefore, the magnesium content is important to the users of industrial water. Magnesium flocculates soil colloids as does calcium and, therefore, enhances the action of calcium.
Magnesium salts act as cathartics and diuretics. The United States Public Health Service (1946) recommends that magnesium should not exceed 125 parts per million in potable water on carriers subject to Federal quarantine regulations (22).
CHAPTER II

CONVENTIONAL METHODS OF ANALYSIS

A. SODIUM

Sodium may be determined gravimetrically by the zinc uranyl acetate method. The main requirement for satisfactory results with this method is good technique. With care, results are accurate and reproducible to ± 2 per cent for sodium concentrations greater than 20 parts per million (22). This method is not as satisfactory as flame photometry for determining low concentrations of sodium.

Flame photometry is rapid and sensitive, but it is subject to numerous interferences. Of special interest is the interference of calcium. Because the calcium emission band at 622 millimicrons is transmitted to some extent, instruments employing light filters are particularly suspect for the determination of sodium in the presence of calcium (20).

To determine sodium in water a radiation buffer can be used. This buffer is prepared by saturating distilled water
with calcium, magnesium, and potassium chlorides. For the
determination one milliliter of the buffer is mixed with 25
milliliters of the water to be analyzed. Photometric mea-
surements are made in comparison with standard solutions
which also contain the buffer (31).

B. POTASSIUM

Potassium can be determined gravimetrically by precipit-
ating it from a mixed solvent as potassium perchlorate.
Potassium perchlorate is only slightly soluble in organic
solvents such as a mixture of n-butyl alcohol and ethyl ace-
tate, while the sodium salt is soluble in such media.
Ammonium salts and sulfates should be absent from the solution.
In the case of sulfate this might involve a preliminary sepa-
ration by precipitation (22).

There is also a standard colorimetric method for potas-
sium. Potassium is precipitated as dipotassium sodium
cobaltinitrite using sodium cobaltinitrite as the precipitat-
ing agent. The precipitate is dissolved in sulfuric acid,
and this solution is used to reduce potassium dichromate.
The color change the dichromate undergoes provides an indirect
determination of the potassium present (22).

Flame photometry is commonly used now for the determina-
tion of potassium in natural waters. However, as in the case
of sodium, this technique is subject to numerous interferences. Sodium, which will invariably be present, enhances the potassium emission. This effect is greatest at low potassium concentrations (20). A radiation buffer, analogous to the type used in determining sodium, can be used (31).

C. CALCIUM

The titrimetric determination of calcium with standard EDTA solution is now commonly used. This method can be applied to most natural waters, but it is unsuitable for many brines and waters which have been polluted with relatively large amounts of heavy metals (22).

A somewhat older, but still often used, technique is the permanganimetric method for calcium. The calcium is precipitated as the oxalate, filtered and washed. The precipitate is then dissolved in acid and titrated with standard potassium permanganate solution. In this method the amount of oxidizable material in the precipitate is measured, and the calcium is calculated assuming the precipitate to be 100 per cent calcium oxalate.

The permanganimetric method is subject to several interferences. The solubility of calcium oxalate is increased appreciably if magnesium is present. This is due to the
formation of a complex magnesium oxalate which reduces the oxalate ion concentration. This difficulty can be surmounted by adding enough excess oxalate to complex all the magnesium present and precipitate the calcium (12). Barium and strontium also form insoluble oxalates. The interference of small amounts of barium may be circumvented by double precipitation, but the strontium interference cannot be removed in this manner. Heavy metals will interfere unless they are removed prior to the addition of oxalate by hydroxide and/or sulfide precipitations (22).

The gravimetric oxalate method is also used for calcium. The precipitation technique is similar to that used in the permanganimetric method except that the precipitate is ignited to and weighed as calcium oxide (27). Weighing calcium oxide is time consuming, especially if the humidity is high. The interferences for this method and the permanganimetric method are similar.

Flame photometry can be used to determine calcium in natural waters. However, filter instruments have low specificity factors for calcium in the presence of sodium and potassium (20). Since these elements will certainly be present, direct flame photometric measurements of the water may give high values for calcium. A common procedure for
obviating the interference of sodium and potassium is the isolation of the calcium as the oxalate, with subsequent dissolution of the precipitate in acid and flame photometric measurement (20). The sodium and potassium interferences can also be eliminated by the use of a radiation buffer analogous to those used for sodium and potassium determinations (31). The flame photometric measurements are usually made at the 554 millimicron CaOH\(^+\) band.

The term "specificity factor" has been introduced as a means of indicating the specificity of a method and instrument. It is the number obtained by dividing the concentration of the interfering element by the concentration of the desired element when the two concentrations are such that both produce the same signal under similar operating conditions (34).

D. MAGNESIUM

There are two "wet chemical" methods in general use for determining the magnesium content of water. In waters for which complexometric calcium and total hardness determinations are satisfactory, the magnesium concentration is calculated by subtracting the calcium parts per million from the total hardness parts per million. If the complexometric method cannot be used, e.g., in the case of brines containing...
barium, the gravimetric pyrophosphate method is used (22).

There are several difficulties encountered in the flame photometric determination of magnesium which preclude the use of this technique in routine water analysis. The atomic resonance line of magnesium lies at 285 millimicrons in the midst of an OH band system. Measurement of this line requires the use of a spectrometer with a quartz prism or a diffraction grating (20). Even with a good monochromator, background corrections are difficult. Filter instruments can be used by measuring the crests of the magnesium molecular bands. The bands extend from 353 to 415 and 490 to 505 millimicrons. However, the specificity factors for these bands are small, in order of 20 for sodium and potassium (7). Also, the band crests are subject to severe spectral and continuum interference.
CHAPTER III

ATOMIC ABSORPTION PHOTOMETRY

A. HISTORICAL BACKGROUND

The phenomenon of atomic absorption has been utilized by experimental scientists for a number of years. Until rather recently its most common uses were the detection of elements in the "cool" gases surrounding stars and the measurement of flame temperatures.

Visual observation of atomic absorption was used to detect the presence of sodium atoms in sodium vapor--alkyl halide flames by von Hartel and Polanyi (10) in 1930. In 1939 Woodson (38) of General Electric designed and patented an instrument for the detection and estimation of traces of mercury vapor in air. This instrument was produced and marketed commercially. Ballard and Thornton (3) constructed an instrument, based on Woodson's design, for the determination of traces of mercury in solution in 1941. The technique lay dormant until 1955 when Walsh (29) demonstrated its broad analytical applicability. Since 1955 between 250 and 300 papers have been published on this subject.
B. THEORY

One of the outstanding features of atomic absorption photometry is that the absorption is proportional to the concentration of ground state atoms, and the concentration of these atoms is not altered appreciably by changes in temperature.

The absorption coefficient, \( \alpha \), is defined by

\[
I = I_0 \exp(-\alpha \gamma b)
\]

where \( I_0 \) is the initial intensity of a collimated beam of monochromatic light, and \( I \) is the intensity after it has passed through a layer of an absorbing medium of thickness \( b \). The absorption coefficient is a function of frequency. No absorption line is infinitely narrow, and no radiation source emits pure monochromatic light. Therefore, the absorption coefficient obtained in practice is an integrated absorption coefficient. If the frequency spread of the light used to make the absorption measurement is small, Equation 1 is still very nearly valid.

Weisskopf and Wigner (30) showed that according to quantum theory, the integrated absorption coefficient of gaseous atoms is

\[
\int_0^{\infty} \alpha \gamma \, d\gamma = \pi \frac{e^2 f}{W mc}
\]
where \( e \) is the electronic charge, \( m \) the electronic mass, and \( c \) the speed of light in a vacuum. The Ladenburg \( f \), or oscillator strength, corresponds to a constant in classical theory which equals the number of electrons per atom which can be excited by the incident radiation. The \( W \) is a quantum mechanical damping term.

If there are \( N_N \) atoms per cm\(^3\) capable of absorption, then the total absorption, \( A \), is

\[
A = \frac{n e^2}{m c} fWN_N b. \tag{3}
\]

The atoms capable of absorption are ground state atoms. Since it is the total concentration of atoms that is of analytical significance, it is necessary to establish a relationship between the concentration of ground state atoms and the total concentration of atoms.

If there are \( N \) atoms at equilibrium at temperature \( T \), and if Boltzman statistics are obeyed, the distribution of the atoms in the different energy states is given by

\[
N_K = \frac{N g_k \exp - E_k/kT}{\sum_K g_k \exp - E_k/kT}. \tag{4}
\]

Here \( N_K \) is the number of atoms in the \( K \)th state, \( g_k \) the statistical weight, and \( E_k \) is the energy of the \( K \)th state.
Examination of Equation 4 shows that most of the atoms will be in the ground state if there are no energy levels near enough to the ground state to have appreciable concentrations at moderate temperatures. In the cases of sodium, potassium, calcium, and magnesium, the first excited states lie between one and five electron volts above the ground state. The flame temperatures used lie between 2000 and 3000 degrees K. Under these conditions, more than 99.999 per cent of the atoms will be in the ground state. Therefore, the concentration of ground state atoms is very nearly equal to the total atomic concentration.

In flame emission photometry, the measured quantity (the emission intensity) is directly proportional to the number of excited atoms. The number of excited atoms varies exponentially with temperature, but the number of ground state atoms remains virtually constant. This is one of the principal advantages of atomic absorption photometry over flame emission photometry.

The width of an atomic absorption line is determined by:

1. The natural width, due to an indeterminateness in the atomic energies. This is a very small width because the atoms have a long life in the ground state.

2. Doppler broadening, resulting from the motion of the atom in the gas.
3. Pressure broadening, due to a reduction in the mean free time between collisions with other atoms.

4. Stark broadening, due to the Coulomb fields of ions or the dipole moments of polar molecules.

The natural line width is of the order of $10^{-4}$ Å, and this is negligible compared with the broadening due to other causes. At 2000 degrees K, the line breadth due to Doppler broadening is still only about 0.01 Å. The small width of these lines presents experimental difficulties in the measurement of the absorption.

In most cases the attenuation of a broad band of light from a continuous source is too small to be measured. If light from a continuous source passes through the gaseous atoms and then enters a monochromator, the resolution required to isolate the absorption line from the continuous background is beyond that obtainable with most spectrographs. Therefore, the common practice of using a continuous source of radiation is not possible using simple apparatus.

Walsh (29) overcame this difficulty by suggesting the use of a sharp-line source. When such a source is used, the exit slit-width need not be of the same order of magnitude as the half-width of the absorption line. The only requirement is the ability to isolate a selected line from other lines emitted by the source.
In most instances vaporization of the sample causes the emission of radiation with the same frequency as that of the source. This difficulty can be circumvented by chopping the source radiation before it passes through the atomic vapor and amplifying the output of the detector with an amplifier tuned to the chopping frequency. The circuit is so designed that the intensity due to this constant background radiation is not registered in the readout system.

The emission line from a hollow cathode lamp is narrower than the absorption line of the gaseous atoms, because the line from the lamp is almost entirely free from Stark broadening. Also, the partial pressure of the atoms in the lamp is less than that in the flame. This results in less pressure broadening for the lamp lines. Therefore, the absorption by the gaseous ground state atoms is affected by anything which broadens the absorption lines. The shape of the absorption curve is not affected appreciably by Doppler broadening, because it varies as $\sqrt{\text{T}}$. Pressure broadening invariably increases as the concentration of gaseous atoms increases, and it presumably causes a reduction in relative absorption. To a first approximation, pressure broadening varies as T.
C. DETERMINATION OF SODIUM, POTASSIUM, CALCIUM, AND MAGNESIUM IN VARIOUS MATRICES

Atomic absorption spectroscopy has been applied to the analysis of sodium, potassium, calcium, and magnesium in matrices other than natural waters. Willis (35, 36, 37) determined all four of the metals in blood serum, and David (4, 5, 6) determined them in plant materials. Allan (2), Robinson (23), Malmstadt and Chambers (17), and Russell, Shelton, and Walsh (24) have described the analysis of aqueous solutions of these metals. Pungor and Konkoly-Thege (21) studied the atomic absorption of aqueous and alcoholic solutions of sodium salts. Methods for determining magnesium in industrial materials such as limestone, cement, and alloys have been developed by Leithe and Hofer (13, 14) and Wallace (28). Newburn (19) determined calcium in saliva by atomic absorption spectrophotometry. Therefore, atomic absorption photometry seems to be particularly well suited for water analysis, since it is rapid, reproducible, sensitive, and free from many of the interferences found in the standard methods.
If atomic absorption photometry is to compete with flame photometry in the field of water analysis, the instrumentation must not be prohibitively expensive or excessively complicated. An atomic absorption photometer consists of all the basic components of a flame photometer plus the light source, light source power supply, and, usually, a modulating system. Therefore, atomic absorption photometers will be more expensive than a comparable flame photometer. However, atomic absorption photometry has some advantages which should justify the added expense.

A schematic of the basic components of the instrument described here is shown in Figure 1. This instrument is simple, relatively inexpensive, and reliable. The components requiring optical alignment (the photomultiplier housing, the burner, and the hollow cathode lamp) are mounted on a Cenco optical bench #85801 for rigidity. The chopper is mounted between the burner and light source on a Flexaframe rack.

No lenses are used with this instrument. The use of
FIGURE 1

BASIC COMPONENTS OF ATOMIC ABSorption PHOTOMETER
lenses in photoelectric photometry is inherently a source of error, since the reading of the instrument usually depends on the adjustment of the lenses. Sufficient sensitivity is obtained without lenses, and the galvanometer reading is not altered by small, accidental displacements of the components.

A. POWER SUPPLIES

A Heath W-PS-4 regulated power supply is used in conjunction with the hollow cathode lamps. The output variation of this unit is less than one per cent for outputs of 100 to 400 volts. A Gates Omnirange power supply and lamp house is used with the Osram lamps. This unit consists of a transformer and current regulating device.

B. LIGHT SOURCES

Hollow cathode lamps are used for calcium and magnesium. These lamps were purchased from Ramsley Glass Instruments of Melbourne, Australia. Osram spectral lamps are used in the determinations of sodium and potassium.

The lamp holder for the hollow cathode lamps is shown in Figure 2. This holder is constructed of 1/16 inch aluminum sheet. The lamp is held securely in the "vees" by two stout rubber bands. The edges of the "vees" are cushioned with pieces of slit rubber tubing. This tubing is held in
\frac{1}{2} \text{ Scale}

FIGURE 2

HOLLOW CATHODE LAMP HOLDER
place with General Electric RTV-102 cement. The lamp holder is mounted on two Cenco optical bench carriages by means of 3/8 inch aluminum rods. Electrical connections are made by means of two binding posts at the rear of the lamp holder.

A lamp house is part of the Gates power unit. A modified mounting rod is used with this lamp house in order that the lamp can be mounted in an optical carriage. The mounting rod is essentially a male adapter tube to pipe. The tube portion is two inches long and 3/8 inch in diameter.

Since the Gates power supply is an alternating current unit, the output from the Osram lamps is modulated at 60 cycles per second; therefore, it is unnecessary to use the chopper with these lamps.

C. CHOPPER

A mechanical chopper is used to modulate the light beam from the hollow cathode lamps. The chopper disk is seven inches in diameter and is constructed of 1/16 inch aluminum sheet. Ten 3/4 inch holes are equidistantly spaced around the rim of the disk. The disk is mounted on a 1/4 inch axial shaft which is attached to the chopper drive by means of a chuck. The chopper drive consists of a 1800 revolutions per minute Bodine motor with a 3:1 reduction gear. The chopping frequency is 100 cycles per second.
If light from the atomic resonance emission spectra of the flame is reflected by the chopper disk into the detector, spectral interference will occur because the rotating disk causes this reflected light to flicker at the chopping frequency. To prevent this interference, the chopper disk is painted flat black.

D. MASK

A circular mask two inches in diameter with a 3/16 inch center hole is cut from 1/16 inch aluminum sheet. It is mounted rigidly to the end of a nine inch length of 3/8 inch aluminum rod by inserting it into a slightly undersize slot and cementing it in place with epoxy cement. The other end of the rod is attached to an optical bench carriage, and this assembly is mounted on the optical bench between the burner and the photomultiplier house. This arrangement insures that all the light reaching the photomultiplier tube from the lamp passes through the flame.

E. BURNER ASSEMBLY

A Beckman large bore, oxy-hydrogen, atomizer-burner #4060 was used for all work described here. Two stage regulators are used on the gas cylinders, and final pressure adjustment is accomplished with a Beckman regulator unit.
The burner is attached to the burner mounting fixture shown in Figure 3. The burner mounting fixture is supported with a six inch length of 3/8 inch aluminum rod. The other end of the rod is set in a Cenco optical bench carriage #85802.

Sample beakers are placed under the burner capillary and raised and lowered by means of a Fisher support jack #14-674-25. The jack is attached to the rails of the optical bench next to the carriage holding the burner assembly.

F. FILTERS

Bausch and Lomb second order interference filters are used in the determinations of sodium, potassium, and calcium. These filters have band half-widths of eight to ten millimicrons and peak transmittances of 35 per cent. The wavelengths, in millimicrons, of the second order transmission bands of the filters are 585 for the sodium filter, 770 for the potassium filter, and 422 for the calcium filter. The sodium and potassium interference filters have third order transmission bands in the visible portion of the spectrum.

The third order transmission bands occur at about 397 and 514 millimicrons in the sodium and potassium filters respectively. A red glass filter with peak transmission at 600 millimicrons is used to block the 397 millimicron band in the sodium filter. Five millimeters of saturated sodium
Full Scale

FIGURE 3

BURNER MOUNTING FIXTURE
dichromate solution is used to block the 514 millimicron band in the potassium filter.

A combination of two filters is used in the magnesium determinations. One is a semisolid nickel sulfate filter as described by Strait, Goyan, and Kumber (28). The other is a Corning 7-54, ultraviolet transmitting-visible absorbing, glass filter. This filter absorbs the visible radiation transmitted by the nickel sulfate filter.

The nickel sulfate filter is made from two ground and polished fused quartz disks three inches in diameter and 1/16 inch thick. These disks are separated by a ring shaped piece of 1/8 inch red rubber gasket material with an inside diameter of approximately two inches. The space between the two disks is filled with a nickel sulfate-sorbitol gel, and the filter is sealed with RTV-102 cement.

G. PHOTOMULTIPLIER HOUSE

The photomultiplier house is shown in Figure 4. The inside is painted flat black to minimize stray light. A one ounce can filled with self-indicating silica gel is placed in the bottom compartment to control the humidity. The leads are soldered to the appropriate tube socket terminals and jacks. General Electric RTV-102 silicone rubber cement is used to coat the exposed wire and solder. The photomultiplier
FIGURE 4

PHOTOMULTIPLIER HOUSE

½ Scale
tubes used are a RCA 1P28 and a RCA 1P22. The forward end of the stray light trap is threaded to receive a model G adapter for a Bausch and Lomb iris diaphragm #31-58-28. The filters are placed over a half inch hole at the rear of the light trap. The area around this hole is covered with black plastic tape to prevent the filters from being scratched. The filters can be held in place by clips similar to those used for microscope slides or with pressure sensitive tape. The 3/8 inch mounting rod fits in a Cenco optical bench carriage.

**H. DETECTOR AND READOUT SYSTEM**

The circuit for the detector and readout system is shown in Figure 5. The electrical and electronic parts are readily available and inexpensive. By using a small number of parts and by operating well below the rated values of these parts, component failure is kept to a minimum.

The capacitor can sustain a maximum potential difference of 450 volts, but the maximum voltage it is subjected to is a few millivolts. Likewise, the maximum current in the rectifier bridge is of the order of one microampere, while the rectifiers are rated at 450 milliamperes. One half watt carbon resistors are used, and all resistors are matched to a tolerance of plus or minus one per cent of the nominal
LEGEND

R - 10^6 Ohms
T - TRIAD A - 40J
S - International Rectifier 5E4-95
1 - 9 - Dynodes                   C - 100 Microfarad
                                         G - Galvanometer
                                         10 - Anode
                                         11 - Cathode

FIGURE 5

DETECTOR AND READOUT CIRCUIT
resistance. Since the photocurrent is very small, the battery life is practically equal to the shelf life. Trouble shooting is essentially reduced to checking the batteries, photomultiplier tube, and electrical connections.

The detector portion of the circuit (dynode resistors and batteries) is coupled to the readout circuit (rectifier bridge, damping capacitor, and galvanometer) with an inter-stage transformer. This transformer has a response range of 30 to 15,000 cycles per second. Therefore, the instrument will respond to any modulating frequency in this range. Experiment has shown that flame flicker is not a source of significant interference.

The electrical parts are housed in a 7 x 8 x 10 inch metal box. The photomultiplier house and the galvanometer are electrically connected to this box with shielded cable and small banana plugs. There are six jacks on the box, three for the leads from the photomultiplier house, two for the galvanometer leads, and one for the ground wire. This wire is connected to a water pipe. The rectifier bridge and the transformer are mounted on a 2 x 7 x 5 inch aluminum chassis base. Two heavy duty single pole single throw toggle switches are incorporated in the circuit. One in between the two 300 volt batteries, and the other turns the current to
the photomultiplier tube on or off. A Rubicon galvanometer is used for the readout. It has a sensitivity of 0.047 microampere per millimeter. It rests on a rubber pad 5/8 inch thick which virtually eliminates vibration problems. A one ounce metal can is filled with self-indicating silica gel to control the humidity in the box.

I. ARRANGEMENT FOR POTASSIUM DETERMINATIONS

The spectral response of the 1P28 photomultiplier tube cuts off at approximately 700 millimicrons. Therefore, it is unsatisfactory for the determination of potassium. A 1P22 photomultiplier tube is used for potassium. However, the 1P22 will not operate satisfactorily in this instrument at 600 volts.

Two small jacks are located on both sides of the toggle switch between the two 300 volt batteries, and they are electrically connected to the leads connected to the switch. When potassium is to be determined, this toggle switch is turned off, and a 90 volt battery, with banana plugs on its leads, is plugged into these jacks. The dynode voltage is now 690 volts, and the 1P22 functions quite well at this potential.
J. THE COMPLETE INSTRUMENT

A photograph of the arrangement of components used for the determination of calcium and magnesium is shown in Plate I, and that for the determination of sodium and potassium is shown in Plate II. The galvanometer has been placed on the detector and readout circuit box in order to get all the components in the photograph. Ordinarily it sits beside the detector and readout circuit box.
<table>
<thead>
<tr>
<th></th>
<th>Plate I</th>
<th>Plate II</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Galvanometer and Detector and Readout Circuit</td>
<td>Galvanometer and Detector and Readout Circuit</td>
</tr>
<tr>
<td>B</td>
<td>Photomultiplier House</td>
<td>Photomultiplier House</td>
</tr>
<tr>
<td>C</td>
<td>Heath Power Supply</td>
<td>Gates Power Supply</td>
</tr>
<tr>
<td>D</td>
<td>Mask</td>
<td>Mask</td>
</tr>
<tr>
<td>E</td>
<td>Chopper</td>
<td>Osram Lamp House</td>
</tr>
<tr>
<td>F</td>
<td>Hollow Cathode Lamp and Holder</td>
<td></td>
</tr>
</tbody>
</table>
PLATE I

ARRANGEMENT OF COMPONENTS FOR THE DETERMINATION OF CALCIUM AND MAGNESIUM
PLATE II

ARRANGEMENT OF COMPONENTS FOR THE DETERMINATION OF SODIUM AND POTASSIUM
A. PREPARATION OF STANDARD SOLUTIONS

All solutions are made up in doubly distilled water. Hereafter, water will mean doubly distilled water. All chemicals used in this work are reagent grade.

Standard stock solutions containing 1000 parts per million of each of the cations are prepared by weight without secondary standardization. The other standards are prepared by making dilution series from the standard stock solutions. All standard solutions are stored in polyethylene bottles. Standards are prepared from oven dried potassium chloride, sodium chloride, calcium carbonate, and magnesium turnings.

1. SODIUM

Reagent grade sodium chloride (2.542 grams) is dried for one hour at 100 degrees C., dissolved in water, and diluted to one liter.

2. POTASSIUM

Reagent grade potassium chloride (1.907 grams) is
dried for one hour at 100 degrees C., dissolved in water, and diluted to one liter.

3. CALCIUM

Reagent grade calcium carbonate (2.498 grams) is dried for one hour at 100 degrees C., dissolved in a minimum quantity of hydrochloric acid, and diluted to one liter.

4. MAGNESIUM

Magnesium turnings are washed with dilute hydrochloric acid, water, and acetone and then dried for 30 minutes in a 100 degree C. oven. One gram of these turnings is dissolved in 50 milliliters of water plus 16 milliliters of 12 molar hydrochloric acid and diluted to one liter.

The other solutions used in this work are used to study interferences. An interference is the diminution or less commonly the enhancement of the absorption of the desired cation by the presence of another substance in the sample. The substance which causes the interference is the interferer. The two general categories of solutions used to study interferences are solutions of interferers and solutions of releasing agents. Releasing agents "release" the desired cation from the influence of an interferer. Both of these types of solutions are prepared by weight without
secondary standardization. These materials are not, in general, primary standards, but the concentrations need not be known with great accuracy. The interferer solutions contain materials which are commonly encountered in natural waters or materials which cause interferences in the conventional methods of analysis. With one exception the interferer solutions are ionic; usually they are salt solutions. These salts are selected so that the counter ion does not interfere.

B. PREPARATION OF INTERFERER SOLUTIONS

The more common type of chemical interference encountered in atomic absorption photometry is anionic interference. Anionic interference test solutions are prepared as follows.

1. CHLORIDE

Oven dried ammonium chloride (1.510 grams) is dissolved in water and diluted to 500 milliliters. This solution contains 2000 parts per million chloride ion.

2. BICARBONATE

Oven dried sodium bicarbonate (1.376 grams) and potassium bicarbonate (1.642 grams) are dissolved separately in water and diluted to 500 milliliters. Each solution contains 2000 parts per million bicarbonate ion.
3. SULFATE

Oven dried ammonium sulfate (1.377 grams) is dissolved in water and diluted to 500 milliliters. This solution contains 2000 parts per million sulfate ion.

4. PHOSPHATE

Oven dried dibasic ammonium phosphate (0.070 gram) is dissolved in water and diluted to 250 milliliters. This solution contains 200 parts per million orthophosphate ion.

5. ALUMINUM (ALUMINATE)

Aluminum foil is washed with dilute hydrochloric acid, water, and acetone and dried in a 100 degree C. oven for 30 minutes. After cooling in a desiccator, 0.883 gram is dissolved in a minimum amount of hydrochloric acid. An additional five milliliters of 12 molar acid is added, and the solution is diluted to one liter. This solution contains 883 parts per million aluminum.

6. NITRATE

A 0.1 molar sodium nitrate solution is prepared by dissolving 8.50 grams of sodium nitrate in water and diluting to one liter.
7. PROTEIN

The only non-ionic interferer solution tested is an egg albumin solution which is used to investigate the effect of protein. Egg albumin (0.025 gram) is mixed with a few drops of water in a mortar and diluted to 250 milliliters. This solution is filtered through Whatman #41 filter paper. If none of the protein were retained on the filter paper, the concentration would be 0.01 per cent protein. However, some albumin is always retained, so the concentration is somewhat less than 0.01 per cent. No preservative is added, and a solution is made up fresh a few hours before checking its effect on the absorption of the desired cation.

The effects of representative heavy metals on atomic absorption are examined because they interfere in the "wet chemical" determinations of calcium and magnesium. These solutions are prepared as follows.

8. BARIUM

A solution containing 1000 parts per million of barium is prepared by dissolving 0.18 gram of barium chloride dihydrate in water and diluting to 100 milliliters.

9. LEAD

A 100 parts per million lead solution is made by
dissolving 0.016 gram of lead nitrate in water and diluting to 100 milliliters.

10. IRON

Iron wire (0.25 gram) is dissolved in a minimum volume of hydrochloric acid, and an additional 20 milliliters of 12 molar acid is added. This solution is diluted to 250 milliliters with water. This solution contains 1000 parts per million iron.

C. RELEASING AGENTS

1. ETHYLENEDIAMINETETRACETIC ACID (EDTA)

Forty grams of the disodium salt of EDTA is slurried in 100 milliliters of water. Sodium hydroxide pellets are dissolved one at a time until all of the EDTA has dissolved. More pellets are dissolved until the solution has a pH of approximately nine. The solution is diluted to 250 milliliters. This solution is 0.5 molar with respect to the disodium salt of EDTA.

2. STRONTIUM CHLORIDE

This solution contains 10 milligrams of strontium chloride per milliliter.
3. 8-QUINOLINOL

Forty grams of 8-quinolinol is dissolved in 40 milliliters of water and 57 milliliters of glacial acetic acid and diluted to 200 milliliters with water.

4. SODIUM CHLORIDE

A 1 molar sodium chloride solution is prepared by dissolving 5.84 grams of the salt in water and diluting to 100 milliliters.

5. POTASSIUM CHLORIDE

A 1 molar potassium chloride solution is prepared by dissolving 7.46 grams in water and diluting to 100 milliliters.

D. TECHNIQUE OF MEASUREMENT

Both the hollow cathode and the Osram lamps require a warm up period before a steady intensity is obtained. In all work done with this instrument a warm up period of one hour is used. The manufacturer's recommended procedure for burner operation is followed. The burner is lighted five minutes before any measurements are made. The shutter is removed from in front of the iris diaphragm at this time, so the photomultiplier operates at the level of intended operation at least five minutes before any measurements are made.
Once the detector, burner, and light source have been optically aligned, all that is required is to aspirate the solutions into the flame and read the galvanometer. Thus, errors due to manipulation are reduced to a minimum. Because of the broad frequency response of this instrument, flame flicker is a source of noise. To minimize this, the burner is placed as far from the photomultiplier house and as close to the lamp as practical. A black, circular mask two inches in diameter with a 3/16 inch center hole is positioned between the burner and the photomultiplier house. This insures that all light from the lamp reaching the photomultiplier house passes through the flame. It also blocks some of the flicker from the flame.

The blank is similar to the standards except it contains none of the desired cation. Blank and samples are alternately aspirated into the flame. Therefore, the sample measurement is made at a time approximately midway between two blank measurements. The average of two such blank values is used as the blank value for the sample. This is particularly important with Osram lamps, because the variations of the output from these lamps is greater than that of the hollow cathode lamps. These fluctuations are much more pronounced at lower lamp currents. Installing a constant
voltage transformer in series with the lamp power supply does not affect the fluctuations, so this is apparently a characteristic of the lamps rather than variations in the line voltage.

Light is completely blocked from the photomultiplier by sliding the shutter in front of the iris diaphragm. The coarse adjustment of the galvanometer is adjusted so that the galvanometer reading is nearly zero. This reading is subtracted from the blank and sample readings.

Absorption is expressed in terms of optical density, D. Let Io be the intensity obtained with the blank and I the light intensity obtained during sample aspiration. Then the optical density is:

\[ D = \log \frac{I_o}{I} \]  

Standards are aspirated into the flame five times, and the average reading for each standard is used in preparing a calibration curve. Samples are aspirated into the flame three times, and the mean value is read from the calibration curve.

E. EXAMINATION OF INTERFERENCES

The concentration of the desired cation is selected so that the optical density obtained with no interfering
substances present lies between 0.2 and 0.7. The ratios of interferer to desired cation are adjusted so that they will be several times greater than the ratios which occur in natural waters. The solutions containing the interfering substance are made up in 25 milliliter volumetric flasks. Appropriate volumes of desired cation and interferer solutions are pipetted into the flasks, and the solution is diluted to volume with water.

The absorption measurements are made exactly as they are for calibration purposes. Two blanks are generally employed. One is for the reference solution which contains only the desired cation and is usually water. The other is the blank for the solutions containing the interferer. The concentration of the interferer in this blank is equal to the highest concentration of interferer used in a test solution.

The efficacy of releasing agents is tested by measuring the absorption of two series of solutions, one of which contains the releasing agent. The control series contains a fixed concentration of the desired cation, and the concentration of the interferer is varied. The other series is similar to the control series except a fixed amount of the releasing agent is added to each solution. One solution in
each series contains no interferer, and these act as reference standards. These two solutions provide three important pieces of data when they are compared to the other solutions in the series. They reveal the extent of interference by the interferer, the effect of the releasing agent on the absorption of the desired cation, and the effectiveness of the releasing agent in removing the interference.

The reproducibility obtainable with this instrument is determined by making a number of measurements from day to day.
A. INTERFERENCES

1. GENERAL

There are three general types of interferences which occur in flame photometry which one might also expect in atomic absorption photometry. Excitation interference (20) occurs when the number of excited atoms in the flame is altered by changing the sample matrix or flame temperature. In principle if the number of excited atoms changes, the number of ground state atoms must also change by the same amount and in the opposite direction. However, since the ratio of excited atoms to ground state atoms is very small, the appearance of disappearance of ground state atoms due to this phenomenon is not measurable. Therefore, atomic absorption photometry does not suffer from this interference. Radiation interference (20) is caused by radiation from the flame near the line to be measured. This interference can be eliminated in atomic absorption photometry by using a chopped light source and a read-out system which responds
only to the chopped light. Chemical interference (20) can occur when the desired cation reacts with another species in the sample solution in such a way that the emission intensity of the desired cation is inhibited. This type of interference also occurs in atomic absorption measurements. Chemical interferences in atomic absorption photometry generally parallel those of flame photometry (11). Since this is the case, the mechanism of interference is probably similar.

The mechanism of chemical interference is not known with certainty. Presumably the desired cation and interferer react to form a refractory substance in the flame. If this substance is not volatilized in the flame, the number of free atoms in the flame, and hence, the optical density of the flame is reduced.

The interferer and desired cation must be present in the same solution in order for interference to occur. Inhibition of flame emission is not observed when the interferers and the sample are introduced into the flame by means of separate atomizers (4, 9, 25). This tends to support the premise that the interference is due to a chemical reaction which occurs during or immediately after the evaporation of the droplet.
The problem of chemical interference has been attacked from three different angles. The interferer can be removed prior to making the absorption measurement (11). This has the disadvantages of adding a source of manipulative error in the determination, and it is time consuming. The interference can be compensated by using standards with composition similar to the sample. This is a good sound practice, but it requires a rather detailed knowledge of the sample. The third method consists of adding an excess of a third substance which will remove the interference or adding an excess of an interferer. Chemical interference is most pronounced at low concentrations of interferer. As the concentration of interferer is increased, the rate of decrease of absorption of the desired cation decreases until a plateau is reached. In the region of the plateau little or no interference occurs with the addition of more interferer, even if the added interferer is a different species, e.g., the interference of aluminum in the determination of magnesium can be removed by the addition of a large excess of sulfate (13). This technique has the disadvantage of lowering the sensitivity of the method.

The manner in which releasing agents overcome chemical interference is not clearly understood. The inhibition of
calcium absorption by phosphate can be overcome by the addition of large excesses of strontium or EDTA in alkaline solution. Inhibition of the emission of the alkaline earth metals is caused by phosphates, sulfates, and aluminum (32). Apparently both calcium and strontium form refractory M-O-P compounds in the flame. It is assumed that strontium competes with the calcium for the phosphate. Since there is much more strontium present than calcium, the amount of phosphate available for reaction with the calcium is reduced greatly, and the interference is eliminated. The EDTA presumably forms a more stable compound with calcium than does the phosphate (7) and shields the calcium from the phosphate.

However, in the last two years, evidence has been brought forth which tends to refute this explanation. The sodium salt of EDTA is a more effective releasing agent than the ammonium salt (35). Baker (8) reports that sodium chloride is more effective than the sodium salt of EDTA. He suggests that the factor controlling absorption is the rate of vaporization of the refractory Ca-O-P particle in the flame. If the particle initially formed by evaporation of the water is an intimate mixture of an alkali chloride and calcium phosphate, the alkali chloride should vaporize very rapidly. When this occurs the Ca-O-P material should be
dispersed as very fine particles, or a highly porous particle is formed. In either case the ratio of surface area to volume is increased, and this permits a higher rate of vaporization.

Wallace (28) offers a similar explanation for the removal of the aluminum interference in magnesium determinations with 8-quinolinol. He believes the exothermic reaction of the 8-quinolinol in the flame ruptures the particle, perhaps explosively. This separates the aluminum and magnesium, and the formation of a refractory mixed oxide phase is prevented.

The extent of an interference or occasionally, even the presence of an interference may depend on the choice of fuel-oxidant mixture. Willis (35) reports that the addition of a large excess of strontium removes the phosphate interference in calcium absorption with an air-acetylene or an air-propane flame, but strontium is not effective with air-coal gas, oxy-acetylene, or oxy-hydrogen flames. Also, the effectiveness in an air-acetylene flame depends on the fuel-air ratio. The type of burner is also an important consideration (32). These factors have resulted in the publication of some seemingly contradictory data from different laboratories.
2. EXPERIMENTAL RESULTS

The results of the experiments with interferers are summarized in Table II. Species which interfere are indicated with a Yes, those which do not with a No, and those which were not tested are marked N.T. The results shown in Table II are not valid for all ratios of interferer to desired cation. However, the experimental ratios are several fold greater than those normally encountered in natural waters. The maximum ratios tested are shown in Table III.

A concentrated solution of any sort will cause a slight decrease in absorption \(^{(8)}\). Presumably, this is due to changes in the density and viscosity of the sample solution. An increase of viscosity will reduce the sample feed rate. The reduction of sample feed rates of concentrated solutions has been experimentally verified.

Mineral acids interfere at moderate and high concentrations, especially with calcium and magnesium. This is in agreement with the findings of other workers \(^{(8)}\). Sulfuric, nitric, and phosphoric acids cause large reductions in magnesium and calcium absorption, but hydrochloric acid interferes only slightly. Apparently the anion is the principal cause of interference. The hydronium ion interferes only slightly or not at all.
**TABLE II**

**INTERFERENCES**

<table>
<thead>
<tr>
<th>INTERFERERS</th>
<th>Na⁺</th>
<th>K⁺</th>
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### TABLE III
INTERFERER-DESIRED CATION RATIOS

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<th>Ca⁺²</th>
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<td>PO₄³⁻</td>
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<td>--</td>
<td>29:1</td>
<td>20:1</td>
<td>69:1</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>9:1</td>
<td>3.5:1</td>
<td>3.5:1</td>
<td>9:1</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>10:1</td>
<td>25:1</td>
<td>8:1</td>
<td>20:1</td>
</tr>
<tr>
<td>Pb⁺²</td>
<td>--</td>
<td>--</td>
<td>2:1</td>
<td>3:1</td>
</tr>
<tr>
<td>Ba⁺²</td>
<td>--</td>
<td>--</td>
<td>4:1</td>
<td>10:1</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>--</td>
<td>--</td>
<td>2:1</td>
<td>5:1</td>
</tr>
<tr>
<td>H⁺</td>
<td>pH 3-4</td>
<td>pH 3-4</td>
<td>pH 3-4</td>
<td>pH 3-4</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>31:1</td>
<td>39:1</td>
<td>40:1</td>
<td>100:1</td>
</tr>
<tr>
<td>Sr⁺²</td>
<td>--</td>
<td>--</td>
<td>200:1</td>
<td>500:1</td>
</tr>
<tr>
<td>OH⁻</td>
<td>pH 10-11</td>
<td>pH 10-11</td>
<td>pH 10-11</td>
<td>pH 10-11</td>
</tr>
</tbody>
</table>
Fortunately, natural waters contain buffers (22) which generally maintain the pH between six and nine, and acids need not be added in order to make the atomic absorption photometric determinations. In the absence of interfering anions, no interferences have been observed in this range.

Cationic interferences are tested by adding the chloride salt to the solution of the desired cation. Strontium chloride is used as a releasing agent. The concentration generally used in this work is four milligrams of strontium chloride per milliliter of sample solution. It causes a slight reduction of the absorption of calcium and magnesium. Judging from the relative amounts of strontium and calcium or magnesium present, the interference is probably due to a change in the physical properties of the solution rather than a chemical interference. Except for strontium, no interference or enhancement of absorption has been observed with the cations tested under the conditions indicated in Table III.

The non-interference of iron, barium, and lead demonstrate an advantage of atomic absorption photometry over classical "wet" methods. These metals interfere with EDTA and precipitation techniques. This is generally of no consequence since all three of these metals occur in concentra-
tions of less than one part per million in potable waters. However, barium and iron occur in certain brines, oil well acidization back flush waters, and some industrial waste waters in sufficient concentrations to interfere with the conventional methods for calcium and magnesium.

Anions are usually added to the sample solutions as ammonium salts. However, sodium and potassium bicarbonates are used to check the bicarbonate interferences, because ammonium bicarbonate is not a satisfactory weighing form. Aluminum is considered an anionic interferer, because the interfering species is probably an aluminate ion \((7)\). It is thought to be formed in the flame by the dehydration of the hydrated aluminum cation.

B. CALIBRATION CURVES

Calibration curves are prepared at the same time the samples are analyzed. This is essential with this instrument because the optical densities of a given set of standards shift slightly from day to day.

It has been observed, in the cases of calcium and magnesium, that small changes in the lamp current, which were barely perceptible on the power supply milliammeter, cause the optical density of a given sample to change. The day to day changes may be due to slight differences in the
lamp current, since it is very difficult to obtain the same lamp current on two different occasions. Also, the lamps probably change with time. Experiments performed by Dowling\(^1\) at Kem-Tech Laboratories showed that the intensity of a hollow cathode lamp varies with the ambient temperature. Since the intensity is known to vary, it is possible that the line width also varies. If this is the case, variations in room temperature might cause variations in the optical densities. Also there may be some variation of sample feed rate due to changes in the gas temperatures and slightly different pressure settings.

As the concentration of the desired cation is increased, the calibration curve bends toward the concentration axis. This has been observed by all investigators. This bending reduces the slope of the curve and thereby limits the concentration range that can be determined without sample dilution. According to Lockyer and Hames (16), who investigated a number of elements, the linear relationship, if it is linear at all, only holds for concentrations below about 20 parts per million. The actual figure varies. The curves vary from one element to another, and they depend on the experimental

\(^1\)F. Dowling, Kem-Tech Laboratories, Baton Rouge, Louisiana, private communication, 1963.
conditions and burner design.

This bending may be due in part to pressure broadening (24). If an atom, during the time it is absorbing radiation, is approached by another atom, the energy levels of the atom in question are altered. This is due to the polarization of one atom by the close approach of another atom. This causes the absorption line to broaden, and less radiation is absorbed in the middle of the line (33). Menzies (18) has assumed that the absorption varies in different parts of the flame, and he has shown that a curved calibration graph logically follows. The absorption certainly must vary in different parts of the flame, and so Menzies' proposal probably accounts for some of the curvature.

C. SODIUM

None of the interferers tested interfere at the ratios indicated in Table III. This is in agreement with the findings of David (5) and Willis (37).

Willis (37) has reduced the sensitivity of the atomic absorption method for sodium by utilizing the 330 millicron resonance doublet. This permits the determination of sodium at higher concentrations than is possible with the 589 millimicrom doublet. The output from a sodium Osram lamp is almost entirely concentrated in the yellow D lines, so the
intensity of the second resonance doublet is very weak. The
detection and readout system of the instrument is not sensi­
tive enough to detect the 330 millimicron doublet emitted
from the Osram lamp, so this method of extending the measur­
able concentration range cannot be used with this instrument.

Because the path length of the flame cannot be readily
diminished, the only simple way to extend the usable concen­
tration range is to reduce the sample feed rate. With gas
pressures of 12 pounds per square inch oxygen and 4 pounds
per square inch hydrogen the usable concentration range is
1-5 parts per million, and with pressures of 4 pounds per
square inch oxygen and 2 pounds per square inch hydrogen this
range is extended to 1-13 parts per million.

The emission intensity of a Ramsley sodium hollow
cathode lamp is so weak that the instrument cannot even
detect the 589 millimicron doublet radiation it emits, so all
measurements have been made with the Osram lamp. The Osram
lamp is operated at 1.3 amperes, which is the manufacturer's
recommended operating current. More sensitivity can be ob­
tained by using lower lamp currents (8), but the output of
our lamp is unstable at lower currents. In as much as all
natural waters have sodium concentrations above one part per
million, sensitivity is not a problem.
A typical sodium absorption curve is shown in Figure 6. This curve is constructed from the mean values of six sets of measurements. The gas pressures in this case were 4 pounds per square inch oxygen and 2 pounds per square inch hydrogen. The average precision of the measurements in the 1-10 parts per million range is ± 0.5 part per million at the 95 per cent confidence level.

An optical density of 0.7 is taken to correspond to the desirable upper concentration limit. At optical densities greater than this the relative error per unit photometric error is large. By the same token the lower desirable concentration limit corresponds to an optical density of 0.23. However, because the galvanometer oscillates less at low concentration than at high concentrations, optical density measurements below 0.23 are more precise than those above 0.7.

Figure 6 shows that the steepness of the curve rather than severe bending imposes the upper concentration limit.

The principal advantage of atomic absorption photometry over flame photometry is the absence of inter-element and spectral interferences. Flame photometry is at least as sensitive and precise (15). A flame photometer with filters would be simpler and less expensive to construct, but since atomic absorption is preferable for magnesium, it is
FIGURE 6

ABSORPTION BY SODIUM
convenient to be able to make all the determinations with the same instrument.

D. POTASSIUM

Potassium, like sodium, is free from chemical interferences at the ratios indicated in Table III.

A typical potassium absorption curve is shown in Figure 7. In the case of potassium, the upper concentration limit is imposed by the curvature of the calibration graph. The absorptivity of potassium is less than that of calcium, magnesium, or sodium, and the desirable lower concentration limit is about 14 parts per million.

This is unfortunate because many natural waters have potassium concentrations lower than this. However, the average precision in the range 2-20 parts per million is about ±0.5 parts per million, and most natural waters will contain at least two parts per million. Therefore, the performance of the instrument is satisfactory from a standpoint of sensitivity and precision. Also, most natural waters contain less than 20 parts per million potassium (22), so the upper concentration limit is not normally troublesome. Probably, in most cases, the water sample can be aspirated into the flame without any prior treatment, except possibly, filtering it to remove particulate matter.
FIGURE 7

ABSORPTION BY POTASSIUM
A Ramsley potassium hollow cathode lamp ceased to function after about three hours of operation. Therefore, an Osram lamp has been used to make all the absorption measurements. This lamp can be operated below the manufacturer's recommended operating current of 1.5 amperes. The lamp is sufficiently stable at 1.0 ampere, the lowest current obtainable with the Gates power supply, to make quite satisfactory absorption measurements.

E. CALCIUM

A typical calcium calibration graph is shown in Figure 8. The usable concentration range is 1-30 parts per million. In the 2-20 parts per million range the precision is ± 0.3 part per million at the 95 per cent confidence level.

Calcium is subject to several chemical interferences. The interferers most likely to be encountered in natural waters are sulfate, bicarbonate, and nitrate. The interferences caused by sulfate and bicarbonate may be removed by using a large excess of strontium chloride or alkaline EDTA. The removal of the interferences due to sulfate and bicarbonate with alkaline EDTA is shown in Figures 9 and 10. The interferences are effectively overcome in both cases. The EDTA concentration, calculated as the disodium salt, is 0.02 molar. In Figure 9 the calcium concentration is fixed at 20
FIGURE 8

ABSORPTION BY CALCIUM
FIGURE 9

SULFATE INTERFERENCE ON CALCIUM ABSORPTION AND ITS ELIMINATION WITH EDTA
FIGURE 10

BICARBONATE INTERFERENCE ON CALCIUM ABSORPTION AND ITS ELIMINATION WITH EDTA
parts per million, and in Figure 10 it is 10 parts per million. The effect of excess strontium chloride on a solution containing a mixture of sulfate, bicarbonate, and phosphate is shown in Figure 11. The strontium chloride overcomes the interferences of all three anions. The concentration of calcium in the solutions is 10 parts per million, and the strontium chloride is four milligrams per milliliter.

Neither alkaline EDTA nor strontium chloride removes the interference due to nitrate. The nitrate interference as well as the interferences due to sulfate and bicarbonate can be overcome with 8-quinolinol. This is in agreement with the observations of Wallace (28).

Phosphate and aluminum also interfere, but they usually occur only at low concentrations in natural waters. Therefore, they can be expected to be less of a problem.

EDTA suppresses the phosphate interference as shown in Figure 12. However, it does not remove the interference. Figure 11 indicates that strontium chloride effectively removes the interference due to phosphate.

EDTA intensifies the interference due to aluminum. Figure 13 shows the removal of the aluminum interference with strontium chloride.

Sodium and potassium chlorides at concentrations of
FIGURE 11

EFFECT OF STRONTIUM CHLORIDE ON THE INTERFERENCES OF SULFATE, BICARBONATE, AND PHOSPHATE ON CALCIUM ABSORPTION
FIGURE 12

PHOSPHATE INTERFERENCE ON CALCIUM ABSORPTION AND ITS SUPPRESSION WITH EDTA
FIGURE 13

ALUMINUM INTERFERENCE ON CALCIUM ABSORPTION AND ITS SUPPRESSION WITH STRONTIUM CHLORIDE
0.2 molar are without effect on the phosphate interference. Baker (8) claims sodium chloride is more effective than EDTA in sodium hydroxide solution. This is probably an instance of contradictory results using different instruments and experimental conditions.

At low concentrations the interferences due to sulfate, bicarbonate, and phosphate are linear. This suggests an indirect method for determining these ions. An indirect method for the determination of phosphate by flame photometry has been known for some time (7). Dowling\(^2\) has developed an indirect method for the determination of sulfate based on its interference with the atomic absorption spectrophotometric determination of lead. However, there are probably few instances when these indirect methods would be the preferred technique.

F. MAGNESIUM

A representative calibration curve for magnesium is shown in Figure 14. The useful concentration range is 1-10 parts per million, and the desirable concentration range is about 3-9 parts per million. The precision at the 95 percent confidence level is about ± 0.6 part per million.

Optical Density

FIGURE 14

ABSORPTION BY MAGNESIUM
More electrical noise is encountered in the determination of magnesium than is the case with calcium, potassium, and sodium. The magnesium resonance line lies in a group of OH bands. A broad band pass filter system is used for magnesium, and it seems probable that the noise is caused by the flicker of these OH bands. This noise reduces the precision of magnesium determinations. Fortunately, the slope of the absorption curve is rather steep, and it is easy to distinguish differences of less than one part per million in the 1-10 parts per million range.

Magnesium is subject to the same chemical interferences as calcium plus an interference due to protein. Figure 15 shows the suppression of the protein interference with strontium chloride. The scatter of the points for the solutions containing strontium chloride is within experimental error.

The effect of 8-quinolinol on nitrate interference is shown in Figure 16. The 8-quinolinol is insoluble in water, so a 25 per cent (by volume) acetic acid solution is used as the diluent. There are two sets of control solutions. In one of the control sets, acetic acid solution is used as the diluent, and water is used in the other. Curiously, the optical density increases with increasing nitrate
FIGURE 15

PROTEIN INTERFERENCE ON MAGNESIUM ABSORPTION AND ITS ELIMINATION WITH STRONTIUM CHLORIDE
FIGURE 16

NITRATE INTERFERENCE ON MAGNESIUM ABSORPTION AND ITS ELIMINATION WITH 8-QUINOLINOL
concentration for the control solutions containing acetic acid. The concentration of 8-quinolinol in the test solutions is 0.9 molar. Strontium does not eliminate the nitrate interference.

The effect of bicarbonate on magnesium absorption is shown in Figure 17. Below eight parts per million bicarbonate does not interfere. Strontium chloride suppresses, but does not eliminate the bicarbonate interference. Bicarbonate interference can always be removed by acidifying the solution and heating. Figures 18, 19, and 20 show the interferences due to sulfate, aluminum, and phosphate and their removal with strontium chloride. The magnesium concentration in Figures 15–20 is four parts per million, and the strontium chloride concentration in Figures 15, 17, 18, 19, and 20 is four milligrams per milliliter.

G. ANALYSIS OF NATURAL WATER SAMPLES

In order to test the suitability of the instrument for water analysis, five water samples have been obtained and analyzed. Four of these are natural river and lake waters which were furnished by the State Water Survey at Urbana, Illinois. The fifth is a synthetic mixture which has been prepared specifically to check the accuracy of mineral analyses of water (15). This water was furnished by the
FIGURE 17

BICARBONATE INTERFERENCE ON MAGNESIUM ABSORPTION AND ITS SUPPRESSION WITH STRONTIUM CHLORIDE
SULFATE INTERFERENCE ON MAGNESIUM ABSORPTION AND ITS ELIMINATION WITH STRONTIUM CHLORIDE
FIGURE 19

ALUMINUM INTERFERENCE ON MAGNESIUM ABSORPTION AND ITS ELIMINATION WITH STRONTIUM CHLORIDE
FIGURE 20

PHOSPHATE INTERFERENCE ON MAGNESIUM ABSORPTION AND ITS ELIMINATION WITH STRONTIUM CHLORIDE
Analytical Reference Service of the Taft Sanitary Engineering Center in Cincinnati, Ohio.

Strontium chloride at a concentration of four milligrams per milliliter is used as a releasing agent in the determination of magnesium and calcium. Sodium and potassium are determined by aspirating the water directly into the flame. The water sample is diluted with redistilled water until the optical density measurements are in a favorable range. The concentration of the desired cation is read from a calibration curve which is prepared at the same time as the determination is made. The concentration found and its uncertainty are multiplied by the dilution factor to obtain the concentration of the desired cation in the natural water. The results of the determinations are shown in Tables IV and V. The concentrations of interfering anions in the waters is given in Table VI.

The water supplied by the Taft Sanitary Engineering Center is the same as that used in a field study made by the United States Public Health Service Analytical Reference Service in 1961 (15). They utilize a concept called the "50 per cent range" to establish the accuracy of a method. This range is defined as the maximum deviation from the amount present for the more accurate half of the determinations.
**TABLE IV**

CALCIUM AND MAGNESIUM IN NATURAL WATERS

<table>
<thead>
<tr>
<th>Water</th>
<th>Found ppm</th>
<th>Dilution Factor</th>
<th>Reported by State Analyst ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaskaskia River, at Shelbyville</td>
<td>Ca-68.5±1.5</td>
<td>5</td>
<td>69.8</td>
</tr>
<tr>
<td></td>
<td>Mg-28.5±3</td>
<td></td>
<td>30.0</td>
</tr>
<tr>
<td>Crab Orchard, at Carterville</td>
<td>Ca-20.5±0.5</td>
<td>1.67</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td>Mg-7.1±0.5</td>
<td></td>
<td>7.2</td>
</tr>
<tr>
<td>Bay Creek, at Nebo</td>
<td>Ca-60.4±1.5</td>
<td>5</td>
<td>60.6</td>
</tr>
<tr>
<td></td>
<td>Mg-14.2±3</td>
<td></td>
<td>14.5</td>
</tr>
<tr>
<td>Wolf Creek, at Beecher City</td>
<td>Ca-42.5±1.5</td>
<td>5</td>
<td>44.1</td>
</tr>
<tr>
<td></td>
<td>Mg-15.3±3</td>
<td></td>
<td>15.7</td>
</tr>
</tbody>
</table>

**TABLE V**

ANALYSIS OF WATER FROM TAFT CENTER

<table>
<thead>
<tr>
<th>Cation</th>
<th>Found ppm</th>
<th>Dilution Factor</th>
<th>Present ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>20.7±1.2</td>
<td>2</td>
<td>19.9</td>
</tr>
<tr>
<td>K</td>
<td>2.9±0.5</td>
<td>1</td>
<td>3.1</td>
</tr>
<tr>
<td>Ca</td>
<td>111±5</td>
<td>10</td>
<td>108</td>
</tr>
<tr>
<td>Mg</td>
<td>80.9±6</td>
<td>10</td>
<td>82</td>
</tr>
</tbody>
</table>
### TABLE VI

CONCENTRATIONS OF INTERFERING ANIONS (ppm)

<table>
<thead>
<tr>
<th>Water</th>
<th>$\text{SO}_4^{2-}$</th>
<th>$\text{HCO}_3^-$</th>
<th>$\text{NO}_3^-$</th>
<th>$\text{PO}_4^{3-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaskaskia River</td>
<td>57.2</td>
<td>142*</td>
<td>13.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Crab Orchard</td>
<td>69.9</td>
<td>19.5*</td>
<td>3.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Bay Creek</td>
<td>28.2</td>
<td>125*</td>
<td>4.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Wolf Creek</td>
<td>41.6</td>
<td>85*</td>
<td>8.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Taft</td>
<td>259</td>
<td>26*</td>
<td>1.1</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Calculated assuming alkalinity is due entirely to bicarbonate.

### TABLE VII

"50 PER CENT RANGES"

<table>
<thead>
<tr>
<th>Cation</th>
<th>&quot;50 Per Cent Range&quot; (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium*</td>
<td>+0.9</td>
</tr>
<tr>
<td>Potassium*</td>
<td>+0.3</td>
</tr>
<tr>
<td>Calcium**</td>
<td>+2</td>
</tr>
<tr>
<td>Magnesium***</td>
<td>+2</td>
</tr>
</tbody>
</table>

*Flame photometric
**EDTA titration
***Calculated
reported. The "50 per cent ranges" for sodium, potassium, calcium, and magnesium are given in Table VII.

The atomic absorption determinations of sodium, potassium, and magnesium lie in this "50 per cent range." The value for calcium is a little high.

The methods indicated in Table VII are the ones which gave the most accurate results in the USPHSARS study, and they are the techniques which are now recommended by the USPHS (15).
CHAPTER VII

CONCLUSION

The atomic absorption photometer described here can be assembled by a person without any particular technical skills. Most of the materials are locally available and fairly inexpensive. The cost of building the instrument, less labor, is about $750. The most costly items are the hollow cathode lamps which cost about $100 each. Educational institutions can obtain Ramsley hollow cathode lamps for about $40 each plus a 43 per cent Customs duty.

The accuracy of this instrument is adequate for routine water analysis, and once the calibration graphs have been made, it is more rapid than the conventional methods for calcium and magnesium. Apparently this instrument gives more accurate results for calcium and magnesium than flame photometry. The "50 per cent ranges" for calcium and magnesium by flame photometry are ± 21 parts per million and ± 18 parts per million respectively (15). In any case, the values obtained with this instrument are well within these "50 per cent ranges."

Chemical interferences are encountered, but they can be eliminated without undue difficulty.
SELECTION BIBLIOGRAPHY


VITA

Charles Bernard Herrin was born on October 31, 1936, in Durant, Oklahoma. He received his elementary education in the public schools of McAlester, Oklahoma and graduated from Duncan High School in Duncan, Oklahoma in May, 1954. He enrolled in the University of Oklahoma at Norman in September, 1954, and received his B.S. degree in chemistry in June, 1958. He entered the Graduate School of the University of Oklahoma in September of 1958, and received his M.S. degree in chemistry in June of 1960.

In September, 1960, he entered the Graduate School of Louisiana State University and is now a candidate for the degree of Doctor of Philosophy.
EXAMINATION AND THESIS REPORT

Candidate: Charles Bernard Herrin

Major Field: Chemistry

Title of Thesis: A SIMPLE ATOMIC ABSORPTION PHOTOMETER FOR WATER ANALYSIS

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

July 25, 1963