



Constant temperature electrothermal atomizers as a solution to matrix interferences in atomic absorption spectroscopy
by Lynn Robert Hageman

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:

The application of electrothermal atomization techniques for atomic absorption spectroscopy has increased many fold in recent years. Along with this widespread application, matrix interferences in pulsed-type electrothermal atomizers have been observed. Until recently, few interference studies have involved constant temperature electrothermal atomizers. In this thesis a comparison is made of interferences in pulsed-type versus constant temperature atomizers for various metals.

During the one to three seconds necessary to heat commercial electrothermal atomizers to the desired atomization temperature, many reactions take place and analyte compounds may be lost from the rapidly heating furnace at varying temperatures with varying matrices—often at sub-optimal temperatures with inadequate atomization, since residence times are short. Thus, matrix interferences are common in these pulsed-type atomizers. However, the same solutions, when atomized in a constant temperature furnace (CTP), show no significant matrix interferences. Lack of ruggedness of analytical procedures using pulsed-type atomizers seems to be an inherent limitation, whereas equipment ruggedness limitations of the GTF are amenable to elimination by appropriate attention to engineering aspects of fabrication. Difficult samples representing common matrices reveal the ease of obtaining interference free results directly with the CTF--and the difficulty, even with pretreatments, of correcting for interferences on a routine basis in pulsed-type atomizers.

CONSTANT TEMPERATURE ELECTROTHERMAL ATOMIZERS
AS A SOLUTION TO MATRIX INTERFERENCES
IN ATOMIC ABSORPTION SPECTROSCOPY

by

LYNN ROBERT HAGEMAN

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of

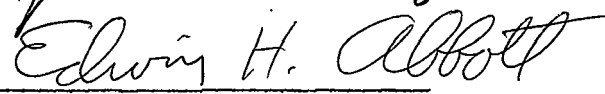
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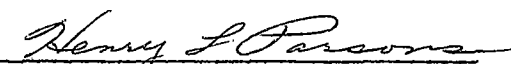
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ABSTRACT

The application of electrothermal atomization techniques for atomic absorption spectroscopy has increased many fold in recent years. Along with this widespread application, matrix interferences in pulsed-type electrothermal atomizers have been observed. Until recently, few interference studies have involved constant temperature electrothermal atomizers. In this thesis a comparison is made of interferences in pulsed-type versus constant temperature atomizers for various metals.

During the one to three seconds necessary to heat commercial electrothermal atomizers to the desired atomization temperature, many reactions take place and analyte compounds may be lost from the rapidly heating furnace at varying temperatures with varying matrices--often at sub-optimal temperatures with inadequate atomization, since residence times are short. Thus, matrix interferences are common in these pulsed-type atomizers. However, the same solutions, when atomized in a constant temperature furnace (CTF), show no significant matrix interferences. Lack of ruggedness of analytical procedures using pulsed-type atomizers seems to be an inherent limitation, whereas equipment ruggedness limitations of the CTF are amenable to elimination by appropriate attention to engineering aspects of fabrication. Difficult samples representing common matrices reveal the ease of obtaining interference free results directly with the CTF--and the difficulty, even with pretreatments, of correcting for interferences on a routine basis in pulsed-type atomizers.

INTRODUCTION

HISTORY

Atomic absorption (AA) has developed into the most widely used technique for analysis of metals and many metalloids ⁽¹⁾ since its introduction as an analytical technique about 20 years ago ⁽²⁾. The widespread use is justified by its versatility, low cost, and high sensitivity. In addition, the high degree of selectivity and relative freedom from interferences are obvious advantages over conventional emission spectrometry. Although considerable research has been aimed at higher sensitivities and lower detection limits, the most ubiquitous and most pressing problem in using the technique is one of matrix interferences - in many cases the response to an analyte in distilled water is simply not the same as the response in a more complex matrix. If all analyte atoms were desolvated, dehydrated, decomposed, and atomized at the same rate regardless of matrix components few interferences would exist ⁽³⁾. This of course has not been the case for flame ⁽³⁻⁵⁾ and most electrothermal atomizers ⁽⁶⁻¹⁰⁾.

Theoretically, electrothermal (ET) atomization is an absolute method of quantitative analysis by AA spectra involving complete vaporization and atomization of a known amount of substance in a graphite cell. In a 1959 publication by L'vov ⁽¹¹⁾ dealing with ET technique of sample atomization, it is concluded that matrix effects

on the results of the quantitative analysis are eliminated, providing considerable advantage over flame version of atomic absorption as well as over the emission methods of spectral analysis. The conclusion was supported by manganese analyses in the presence of NaCl $\text{Pb}(\text{NO}_3)_2$, and $\text{Sr}(\text{NO}_3)_2$. Subsequent publications (12, 13) also indicated absence of matrix effects. But since that early work, numerous publications have appeared in the literature (14-18) dealing with significant and varied interference problems associated with ET atomization for AA spectroscopy. If L'vov's early findings with electrothermal atomizers are correct, interference problems are now present in a technique which theoretically should not have interference problems.

The history of electrothermal atomization use with atomic absorption spectroscopy can be divided into two periods. The boundary between the two periods is sometime in the late 1960's. The first period witnessed the emergence of electrothermal atomization, development, and use by research teams on laboratory designed equipment. The second period, involved the rapid spread of ET atomization methods in analytical laboratories as a promising method of microanalyses due to the advent of commercially available equipment.

Excellent work was done during the first historical period by L'vov in Russia. L'vov developed a graphite atomizer which involves

a graphite tube (40 mm by 2.5 mm) held constantly at a high temperature in the optical path of the AA instrument (see Figure 1,a). The graphite tube is heated to the desired temperature and maintained at this temperature by an electric current and resistance heating. The samples contained in a small carbon cup, are brought to an opening in the side of this tube and heated to attain vaporization and atomization by a separate power supply. The entire atomizer is enclosed in a chamber pressurized with argon. This chamber must be depressurized and the carbon tube must be cooled before the next group of samples can be introduced to the chamber. Extensive work has been done with this type of atomizer attaining very good absolute sensitivities and as has been stated previously with very few matrix effects.

At about the same time that L'vov was developing his graphite atomizer, a similar type was developed by Woodruff and associates at Montana State University (19-21). It is similar to that of L'vov's in that the graphite tube is maintained at constant temperature in the optical path by resistance heating (Figure 1,b). The sample, introduction, on the other hand, is at atmospheric pressure against a stream of argon. The Woodruff Constant Temperature Furnace (300 mm by 7 mm) is also larger than that developed by L'vov. No auxiliary power supply is necessary for the volatilization of

sample. A stream of argon is also used to flush the graphite tube as a means of preventing oxidation.

During this period, Massmann in Germany⁽²²⁾, also developed an electrothermal atomizer. This atomizer consisted of a graphite tube 55 mm long with an inside diameter of 8 mm supported at the ends by water cooled electrodes (Figure 1, e). It employs a different mode of operation than the two ET atomizers discussed previously. The sample is placed in the tube at room temperature. A three step program is then employed - drying the sample near 370 K, ashing the sample from 370 to 1800 K depending on the matrix and finally, atomizing at temperatures as high as 3300 K. A sheath of Ar or N₂ is used to reduce reaction with O₂ in the air.

At the onset of the second historical period, when electrothermal atomizers became readily available through commercial production, the companies involved opted to use the most simple equipment and technique, which is the Massmann design. The Massmann design was adopted essentially without change by Perkin-Elmer Instrument Company, and a mini-Massmann ET atomizer was developed by Amos and Matousek⁽²³⁾ and adopted by Varian Techtron Instrument (Figure 1, d). The mini-Massmann or carbon rod atomizer (CRA) is operated with the same type of three step program as the Massmann, but is much smaller in size (9 mm long with an inside diameter of

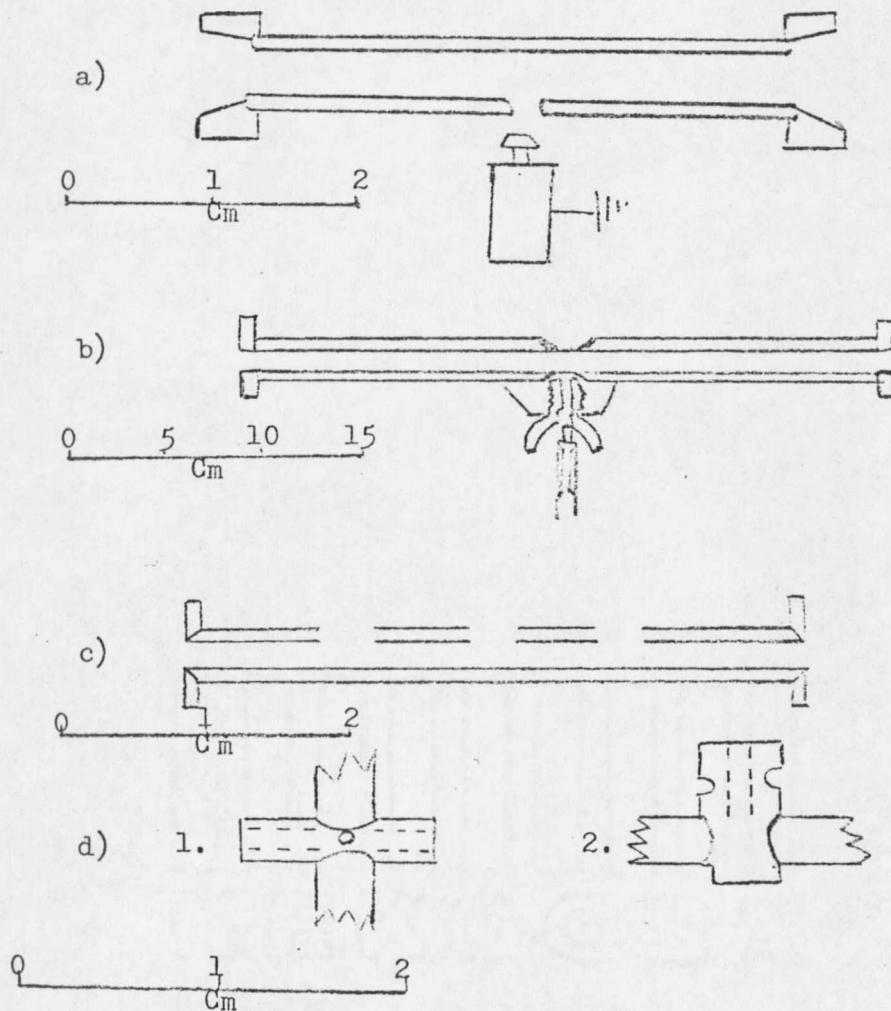


Figure 1. Electrothermal atomizers

- a) L'vov Constant Temperature Furnace
- b) Woodriff Constant Temperature Furnace
- c) Massmann Pulsed-Type Atomizer
- d) Varian Mini-Massmann Atomizer
 - 1. Carbon Rod Atomizer
 - 2. Carbon Cup Atomizer

3 mm). There have been some other ET atomizers developed since 1970 such as, Instrumental Laboratories graphite furnace, but the present state-of-the art of ET atomizers is still divided into two types. The first being the constant temperature type where the atomizing chamber is held constantly at optimum atomization temperature and the samples are introduced to it. The second type includes the commercially available ET atomizers using a pulsed-type mode of operation; i.e., introduction of sample at room temperature, drying, ashing, and finally volatilizing and atomizing under condition of rapidly increasing temperature. Although "electrothermal" is probably the most descriptive nomenclature, during the first period electrothermal atomizers were generally referred to as furnace atomizers and the first commercial electrothermal atomizers were referred to as "flameless" or "nonflame", as opposed to previous "flame" atomizers. Therefore, occasionally in this thesis when referring to previous literature reports, the terms furnace or flameless atomizer are used interchangeably with electrothermal atomizer.

The commercial atomizers were accepted enthusiastically during the early 1970's with expectations of analytical applications to essentially all metals in any type of sample. Many methods were published, especially by instrument companies, with no mention of interferences. However, perusal of the ever-growing number of

recent publications in the field of AA analysis using ET atomization of samples, it could be concluded that, unfortunately, ET atomization has not lived up to this high expectation. Rather, the reverse has taken place, a disappointment exists regarding the possibility of ET atomizers for complete atomization and absolute methods. In fact, the trend in recent literature is toward cataloging the many matrix interferences that are observed and then working out an organic chelation and extraction, matrix modification, coprecipitation, or standard addition to alleviate the problem. All these techniques involve time, possibility for contamination, and often are applicable only to a specific type of sample. Also reported recently is an unpredictable dependence of sensitivity on the conditions of measurement such as: heating mode, position of the sample in the furnace, gas flow rate, age of tube, etc. This has led up to statements such as: "...It has become apparent for sometime that the greatest barrier to the acceptance of flameless atomization as a normal tool in atomic absorption spectrometry is its susceptibility to matrix interferences⁽²⁴⁾". Such statements resulted in the contention that electrothermal atomizers, in general, are very susceptible to matrix interference, an opinion which is contradictory to theoretical evaluation and optimistic forecast of the early publications.

STATEMENT OF THE PROBLEM

The purpose of this work was to establish a matrix interference comparison of commercially available ET atomizers to the constant temperature ET atomizer developed at Montana State University. The comparison was made on the basis of data accumulated in this laboratory, some of which has already been reported in recent literature, and on data reported in the literature by other investigators. Through this comparison, it was intended that a better understanding of the mechanisms and causes of interferences in the pulsed atomizers would be derived. Several elements, representing a broad spectrum of properties, have been used to accomplish this comparison. The instrumentation and experimental set up allowed for direct comparison on the same solutions with the atomizer being the only significant variable.

INTRODUCTION TO MATRIX EFFECTS

There are several general considerations to take into account when considering possible ways in which matrix materials can affect analyte absorption signals. Chemical matrix interferences can have an effect on the rate of atomization of the analyte. This influences the sensitivity in two ways. First, absorption can be lowered because some of the atoms may have time to leave the light path before the last evaporates. Second, a change in atomization rate can also

change the time at which the maximum analyte atom concentration enters the light path. In pulsed-type atomizers, where the temperature is changing rapidly, this means that the peak reading will be taken at different temperatures depending on the matrix elements. Absolute sensitivity in general varies with temperature, that is if atomization is delayed until the temperature has increased, the diffusion rate will also have increased and less absorption will be observed than at lower temperatures. Chemical interferences may also be attributed to formation of compounds which are volatile at the temperatures attained in ET atomizers, but yet have enough stability to escape without atomization. This could include either a recombination of analyte atoms with interferences, or a lack of dissociation of volatile analyte containing compounds before atomization temperature is achieved. Chemical interferences such as these will receive the most attention in following discussion, but there are other ways in which matrix materials affect analyte absorption of which the investigator need be aware.

For example, as the matrix becomes gaseous it tends to sweep the analyte out of the chamber. A long chamber helps to minimize loss of analyte. Another physical effect which may be an extreme of the first, involves the loss of agglomerates of matrix with analyte trapped in them during the period of rapid volatilization and

expansion. Compound formation with the walls of the atomizer is thought to be responsible for matrix effects when certain elements such as boron or tungsten are involved in the matrix.

Matrix materials can also cause interferences by broad band absorption (background absorption) and scattering of light from condensed particles. Effective methods have been developed for avoiding these two types of nonatomic absorption except for excessive background absorption that occurs with some organic matter⁽²⁵⁻²⁷⁾. Most techniques used to correct for non-atomic absorption involve its measurement by use of a continuum lamp source such as hydrogen or deuterium hollow cathode lamps. This absorption is then subtracted from the total absorption measured when using the elemental hollow cathode lamp of the analyte. The total absorption minus the nonatomic absorption is then equal to the atomic absorption of interest. Most of the early work with electrothermal atomizers therefore, involved introduction of the sample twice to obtain a single atomic absorption. One measurement is made with the elemental lamp in place to measure the total and one with the continuum lamp to measure nonatomic absorption. In this work, total and nonatomic absorption were measured on one sample introduction by a technique of simultaneous background correction. When using this technique, light from both the continuum and elemental lamp are

directed along the optical path by means of beam splitter. The current through the two lamps is adjusted to provide equal intensity. The two lamps are pulsed out of phase so that the lock-in amplifier which is designed to detect only the AC signal will output only the atomic absorption with the nonatomic absorption already subtracted electronically.

EXPERIMENTAL

INSTRUMENTATION

Several instruments were employed in collecting the data presented in this thesis. A Varian AA-5 spectrophotometer equipped with an IM-6 lock-in amplifier conversion module, BC-6 simultaneous background corrector, model 63 carbon rod atomizer, and a Beckman model 1005 strip chart recorder was used for collection of most of the data involving the carbon rod atomizer. A Varian AA 1150, also with simultaneous background correction and a model 63 carbon rod atomizer was used at times for confirmation of the results. This was done to assure that a certain interference was not just a characteristic of the instrument being used, but was indeed a characteristic common to the mini-Massmann model 63 CRA.

Most of the comparison data for the constant temperature electrothermal atomizer that is shown in the charts and figures was been obtained when using a Varian AA-6 spectrophotometer equipped with a BC-6 simultaneous background corrector, a Beckman model 1005 strip chart recorder, and the constant temperature ET atomizer developed at Montana State University. Some minor adaptations were necessary to allow convenient use of the CTA in the Varian AA-6. These modifications involved raising the ends of the spectrophotometer to allow access to the bottom of the constant temperature

atomizer (CTA) for sample introduction, removal of the housing which normally encases the flame area, and removal of the lens which normally focuses light on the entrance slit of the monochromator (Figure 2). A focusing lens is included in the exit end cap of the atomizer to avoid use of the extra lens. This instrument is excellent for the comparison data because the electronics and monochromator are exactly the same as the updated AA-5 used to collect the CRA data. The only difference between the two instruments is the ET atomizer.

Much of the preliminary data using the CTA was obtained on an instrument constructed by combination of available components within the laboratory. These components included a Beckman DU quartz prism - spectrometer equipped with a photomultiplier attachment, a Heathkit D.C. power supply, and a Varian AA-5 lock-in amplifier to provide photomultiplier voltage and output of the absorption signal. The AA-5 amplifier was adapted to enable simultaneous background correction by addition of a logarithmic amplifier for combination of the transmission signals before converting to absorption. A NAND gate was also added to provide a hollow cathode pulse which is 180° out of phase with the normal hollow cathode pulse (28). Electronic circuitry was constructed to enable the AA-5 amplifier pulses to control the Heathkit D.C. power supply for the hollow

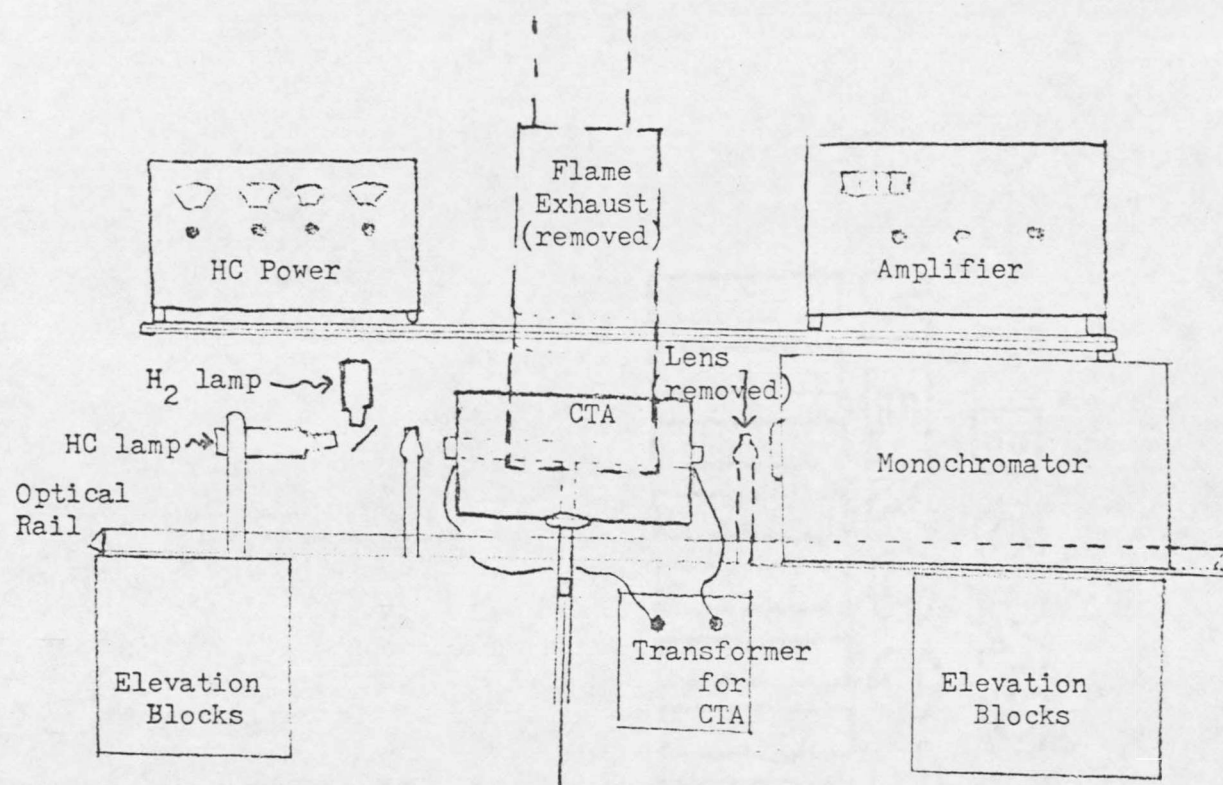


Figure 2. AA-6 Adapted for use with Constant Temperature Furnace.

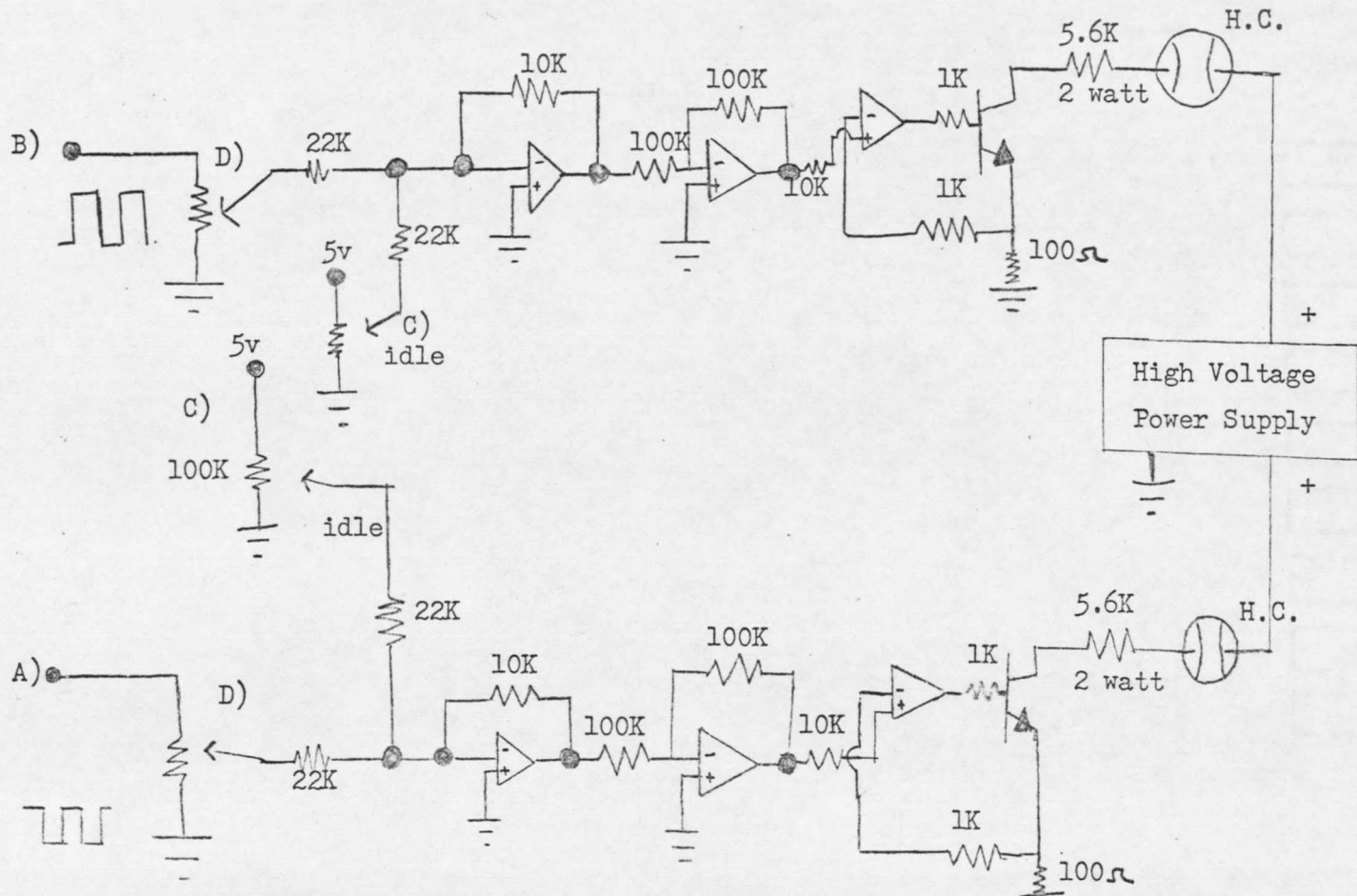


Figure 3. Circuit for control of high voltage to hollow cathode lamps.

cathode lamps. The circuit is shown in Figure 3. This is a two channel circuit to allow for control of two hollow cathode lamps (H_2 lamp and element lamp). The incoming pulses are the normal AA-5 pulse (A) and the out of phase pulse from the NAND gate (B). Therefore, the lamps will be pulsed 180° out of phase by the identical circuits involving several operational amplifiers required for compatibility with the transistor. The TR 60 transistor is necessary for pulsing the high voltage (up to 400 volts) from the Heathkit power supply to the hollow cathode lamps. Two ten-turn pots are used in each channel for controlling the DC idle current (C) and the pulsed current (D).

In addition to the strip chart recorders used, a digital integrator was used for obtaining the area of the absorption signals for both types of ET atomizers. The integrator was constructed with an operational amplifier, voltage-to-frequency converter, and a digital counter. A diagram of the circuit is shown in Figure 4. AA-5 and AA-6 amplifiers both have a 10 mv and 100 mv output. The recorders used in this work have a 10 mv input so that the 100 mv output of the amplifier is available for input to the integrator with no interaction with the recorder. The voltage-to-frequency converter has a linear operation range from 0-10 volts. Therefore, an operational amplifier is used to provide a gain of 100 and a follower amplifier is used to isolate the signal.

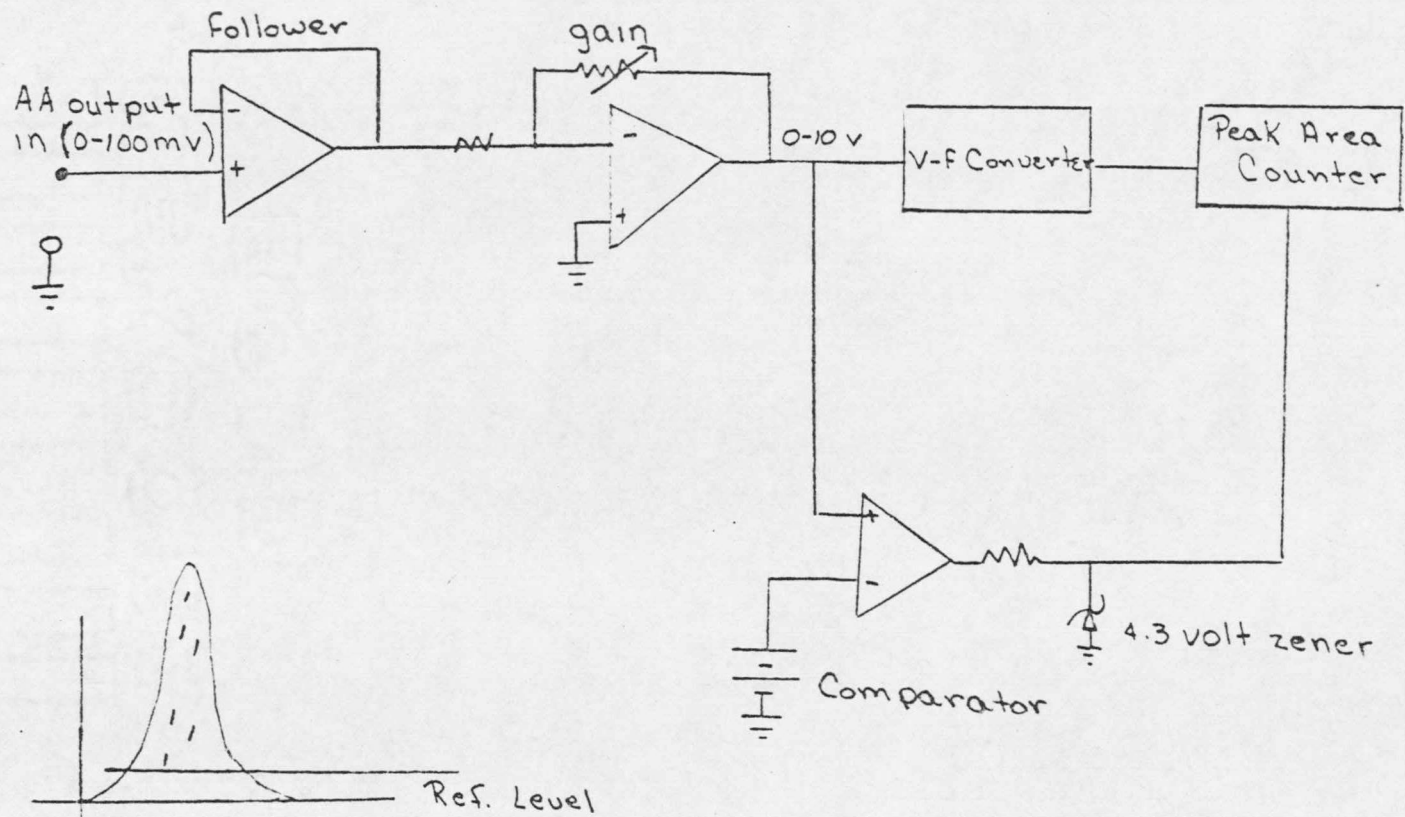


Figure 4. Schematic of integrator.

A reference voltage is established above the noise level at which the comparator starts and stops the digital counter. The number of counts obtained as pulses from the voltage-to-frequency converter is directly proportional to the input voltage, thus directly proportional to peak area. This is illustrated in Figures 5 and 6 by plots of input voltage for a known period of time versus counts, and by a plot of counts versus weight of chart paper for several peaks.

Temperature measurements for the CTA were made with a Pyro-optical pyrometer. Temperature is difficult to measure for the CRA because it can be changing by as much as 800 degrees per second. Therefore, CRA temperature was estimated by combining optical pyrometer readings and plots of temperature versus instrument setting in the Varian manual.

The CRA was operated according to the manufacturer's specifications and directions; ash and atomization temperatures were optimized to minimize interferences. One modification to the manufacturer's instructions is that methane was added to the sheath of N_2 during the ashing and atomizing cycles. The purpose of the methane was to assure a reducing atmosphere and to maintain a pyrolytic coating on the carbon atomizer tube. The presence of methane causes only a slight increase in background, which is adequately compensated

