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A NEW BACKGROUND-CORRECTION METHOD FOR ATOMIC
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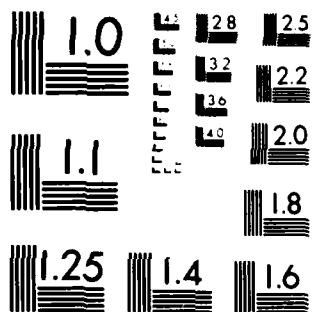
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20. (continued)

required and working curves are single-valued. The new technique is based on the broadening which occurs in a hollow-cathode spectral line when the lamp is operated at high currents. Under such conditions, the absorbance measured for a narrow (atomic) line is low, whereas the apparent absorbance caused by a broad-band background contributor remains as high as when the lamp is operated at conventional current levels. Background correction can therefore be effected by taking the difference in absorbances measured with the lamp operated at high and low currents. The new technique is evaluated in its ability to correct several different kinds of background interference and is critically compared with competitive methods.

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OFFICE OF NAVAL RESEARCH

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A NEW BACKGROUND-CORRECTION METHOD
FOR ATOMIC ABSORPTION SPECTROMETRY

by

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Prepared for Publication

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INTRODUCTION

In most routine applications of atomic absorption spectrometry, it is important to employ a background-correction scheme. Especially when electrothermal atomization is utilized, background correction is necessary to avoid errors caused by molecular absorption or scattering of the incident source (hollow-cathode lamp) radiation. Without such correction, the background absorber is indistinguishable from the element being sought and produces calculated values of elemental concentrations which are too high.

Methods which have been developed for background correction rely upon the spectral difference between narrow-band elemental absorption lines and the broad-band character of either molecular absorption or particulate-caused scattering. The most common of these methods employs an auxiliary source, ordinarily a deuterium arc lamp, which measures principally broad-band absorption (1). Subtracting the absorbance measured with the deuterium lamp from that obtained with a hollow-cathode lamp then provides a high degree of freedom from background absorption or scattering effects. Another, more recently introduced technique for background correction in atomic absorption employs the Zeeman splitting of atomic lines (2-4). In the Zeeman approach, an external magnetic field is utilized to separate spectral lines into their otherwise degenerate components. Conveniently, these components have different polarization characteristics and can therefore be examined sequentially using a rotating linear polarizer. Isolation of elemental absorption from molecular absorption or scattering then relies upon the magnetic and

polarization characteristics of the atomic lines.

Unfortunately, both the deuterium-arc and Zeeman methods for background subtraction suffer several practical drawbacks. Specifically, the deuterium-arc technique requires careful alignment of optical components, an auxiliary source, and benefits from a double-beam optical system. Moreover, the auxiliary source must be replaced occasionally, is relatively expensive, and is not particularly useful in the visible region of the spectrum. Similarly, the Zeeman approach suffers from the need for an auxiliary magnet and relatively sophisticated instrumentation, and from the possible production of double-valued working curves. In addition, because of problems encountered with source (hollow-cathode lamp) instability in the presence of a magnetic field, and the difficulty of applying an electric field to an analytical flame, the method is ordinarily useful only with an electrothermal atomizer.

What would be desired is a background-correction scheme which utilizes the same, simple, single-beam optical system encountered in a conventional atomic absorption spectrophotometer. Also, it would be best if no additional sources were required and that the method could be applied to either flames or furnace atomizers. Finally, background correction should be possible, as in Zeeman instruments, very near the atomic line of interest, so that strongly sloping backgrounds could be overcome.

In the present paper, a new arrangement for background subtraction is described which possesses most of the above-mentioned attributes. The technique is similar to the deuterium-

arc arrangement in concept, but can operate in a single-beam mode and uses only a single source--the hollow cathode lamp ordinarily supplied with an atomic absorption instrument.

The new system functions by operating the hollow-cathode lamp in a double-pulsed mode. An initial, low-current pulse produces an emission line from the hollow cathode which is similar to that ordinarily employed in atomic absorption spectrometry and provides a combined measure of atomic and background absorption. In contrast, a second, high-current pulse produces from the hollow cathode a broadened spectral line which is somewhat self-reversed. As a consequence, absorbance measured during the high-current pulse consists principally of that produced by background absorbers. Subtraction of absorbance values measured during the two pulses then provides a background-corrected signal.

In this manuscript, it will be shown that careful control of the current waveform enables excellent correction of errors which would otherwise be caused by broad-band scattering, molecular absorption, and even atomic-absorption spectral-line overlap. Moreover, because the average lamp current is extremely low (approximately 4 mA), hollow-cathode-lamp lifetime is not significantly degraded and, for most elements, exceeds 5,000 mA-hr. Finally, precision and detection limits obtainable with the new background-correction technique are shown to be comparable to or better than those obtained with competitive methods and approach those expected for single-beam atomic absorption measurements.

I. EXPERIMENTAL

A dual-double beam atomic absorption spectrophotometer (Model 951, Instrumentation Laboratory, Inc., Wilmington, MA) was adapted for these studies by changing the hollow-cathode power-supply control circuit and the analog portion of the signal-processing circuit. The hollow-cathode (H.C.) supply changes consisted of the addition of a second controlled-current mode capable of supplying brief, high-current pulses to the hollow-cathode lamp. The preamplifier (analog signal processor) was altered to allow separate integration, logarithmic conversion and digitization of the various light signals. For comparison with the new background-correction method, the deuterium-arc background corrector ordinarily supplied with the spectrophotometer was retained.

The modified hollow-cathode drive circuitry is shown schematically in Fig. 1. The desired current levels for the high-current and low-current modes are set by potentiometers R_1 and R_2 , and the idle current is set at the input of amplifier A2. The solid-state switch (Analog Devices 7511) is program-controlled to generate the 9-ms low-current pulse, the 0.3-ms high-current pulse and the 1-mA idle current. The general drive-voltage waveform is shown below amplifier A1. The multiplexer amplifier (MUX) is used to gate the signal waveform at desired points (phase angles) so that the various H.C. currents can be sampled and held in the "sample-hold" (S/H) amplifier and measured by a front-panel meter (M).

Amplifiers A1-A4 are contained on a single-chip TL084. Amplifier A1 is used as a follower to sum into A2 the desired

waveform. Amplifier A4 senses the voltage being dropped across the 8.2-ohm resistor and generates a voltage (V_i) proportional to the current flowing through the hollow-cathode lamp. The voltage V_i is compared to the desired voltage at the input of amplifier A3 and the required drive is impressed on the power F.E.T. that controls the hollow-cathode current. Filters on amplifier A3 are used to achieve fast but stable response since the H.C.L. must settle and be stable within 0.1 ms. Current regulation is precise to better than 0.05%.

The preamplifier and analog-conditioning amplifiers are shown schematically in Fig. 2. The photomultiplier (P.M.T.) current is translated into a voltage by A1. The gain is switched as required to accommodate the wide P.M.T. current range that is expected (2 nA to 300 μ A).

A zero-restore (Z/R) amplifier has been used to correct for P.M.T. current offsets caused by light emitted by a flame, hollow-cathode emission during its idling stage, by dark current in the P.M.T. and by offsets in the amplifiers. During the hollow-cathode idle condition the zero-restore integrator amplifier (Z/R) is connected to the output of A1 and charges to a voltage which, when applied to the input of A1 through a resistor, exactly compensates for all dc offsets. Before the H.C. current is raised, the Z/R amplifier input is opened so the offset correction remains applied to A1. The H.C. current is then raised to the "low-current" level and, after a settling period of 0.1 ms, integrator A2 integrates the voltage from A1 for 9 ms. Integrator A2 is then disconnected from A1, the H.C.

current raised to the "high-current" level and, after 0.1 ms, A1 is connected to A3 for 0.2 ms. The gains of A2 and A3 are adjusted to produce an output integral of 10 volts when the hollow-cathode lamp is observed unattenuated (P_0 value).

Integrator A2 is then connected by the MUX and follower amplifier to a logarithmic amplifier (LOG). The gain of the log amp is such that a full scale (10 volts) input generates a 0 volt output; the log amp responds with a slope of 1 volt/decade. Hence an absorbance of 3.4 will yield a 3.4-volt output from the log amp. Amplifier A4 sums a 10-volt offset with the log-amp output and has a gain of about 3. The signal is offset so that the 10-volt input to the V/F represents the "high" light level state, in order to achieve the highest count resolution at the condition of maximum light, i.e. the zero absorbance state. The output of A4 is connected to a voltage-to-frequency converter (V/F) with a maximum output frequency of 2 MHz at an input of 10 volts. A counter receives the V/F output and is gated to accumulate pulses for a period of 5 ms, so a full-scale count of 10,000 is achieved. The counter register contents are then transferred to a FIFO (first in/first out) register. Integrator A3 is next connected by the MUX to the log amp and the integrated voltage digitized in the same manner as for A2. Because integrator A2 is reset as soon as its signal has been digitized, it is free to start integrating the next signal immediately. Therefore, the two signal processing steps (A2 and A3) can be performed more or less simultaneously.

As the various log intensity signals (I_{low} , I_{high} , $I_{o\ low}$, $I_{o\ high}$) are digitized and stored in the FIFO, the controlling

microcomputer transfers them into memory locations. The FIFO is then ready to accumulate the next cycle's data while the computer reduces the log intensity values to concentration equivalents by comparison to pre-established calibration curves.

In a photon-limited spectrometer, the noise in the measurement is proportional to the square root of the number of photons detected. When two measurements are made, it is desirable to equalize the number of photons in the two in order to minimize the total noise contribution. Using this criterion, integration times were selected to yield the same approximate number of photons in each current-level mode.

The pulse-cycle repetition rate that was selected in the present study allows the atomic cloud generated in the H.C.L. during the high-current mode to clear before measurement is made in the low-current mode. Earlier workers (5) have shown that the atom cloud in front of some hollow cathodes dissipates in a few ms. However, lamps of Ag, Cd, and Cu tested in the present study exhibited a persistence of the vapor cloud for more than 6 ms. In contrast, atomic absorption signals revealed that the Pb spectral profile returned to its narrow, low-current shape in this same period. To encompass the broad range of elements determined by atomic absorption spectrometry, we ultimately adopted a cycle period of 50 ms; by this time, only the Cd lamp exhibited an appreciable residual line broadening. This residual broadening was judged not to adversely affect atomic absorption signals.

II. RESULTS AND DISCUSSION

The basis for the new method of background correction lies in the broadening of the emission line from a hollow-cathode lamp when that lamp is operated at high currents. This broadening, for both DC and pulsed currents, has been examined by several workers (6-8); its effect on atomic absorbance is revealed in Fig. 3. In Fig. 3, the apparent absorbance of a constant concentration of cadmium atoms in a air-acetylene flame is shown to decrease as the hollow-cathode primary source is operated at progressively higher currents. This absorbance decrease is caused by broadening of the hollow-cathode emission lines at higher currents, where a greater fraction of the emitted radiation falls outside the absorption band of the cadmium atoms. This unabsorbed fraction of radiation causes the hollow cathode lamp to behave somewhat like a continuum source, reduces the calculated absorbance value, and would produce the bending of working curves which one associates with continuum-source atomic absorption (9,10). In fact, under extreme conditions of operation, a sufficient concentration of cadmium atoms can be built up within the hollow-cathode lamp that the emission line becomes self-reversed (7). Such a self-reversed line profile is compared schematically with a conventional hollow-cathode lamp profile in Fig. 4.

The emission-line profiles portrayed in Fig. 4 suggest how this single source--a hollow cathode lamp--can be employed for background correction in atomic absorption spectrometry. The line profile emitted under low-current operation would be

extremely narrow and would be affected equally by atomic absorption or a broad-band spectral feature and illustrates the problem one ordinarily encounters in atomic absorption when no correction procedure is utilized. In contrast, the profile obtained at high current will be affected more strongly by a broad-band absorber or scatterer than by atomic absorption, much in the same way the detected profile of a deuterium lamp is affected. Absorbances calculated under low-current and high-current operation can then be subtracted to yield a difference value which should be relatively free of any broad-band contribution.

The utility of this novel scheme is apparent from Fig. 5, where working curves obtained under low-current and high-current operation are reproduced. To generate the curves in Fig. 5, no background absorber was present, and the reduced apparent absorbance obtained during the high-current hollow-cathode pulse is evident. Importantly, the difference between the high-current and low-current working curves, labeled "delta", has a somewhat lower slope than the curve generated at low currents, suggesting a slight loss in sensitivity for the new method. The consequence of this loss will be considered in detail later.

Not plotted on Fig. 5 is the expected effect of a broad-band absorber or scatterer. Because of the broad-band character of these sources of interference, one would expect the apparent absorption they produce to be the same regardless of the hollow-cathode lamp emission profile. Therefore, at any expected concentration of interferent, the absorbance values calculated for high-current and low-current operation of the hollow-cathode

lamp should be identical. Consequently, subtraction of the two absorbances will exactly cancel the contribution from broad-band interferents, but will yield a difference value which is proportional to analyte concentration .

Obviously, for this new approach to be effective, it is necessary to broaden appreciably the emission line of each element under investigation. In turn, the degree of broadening of each element will be different and will depend upon the peak current at which the hollow-cathode lamp is driven. To achieve the desired degree of line broadening while maintaining hollow-cathode lamp reliability and longevity requires a careful selection of current waveforms. After examination of a number of such possible waveforms, the one shown in Fig. 6 was adopted. During operation, the hollow-cathode lamp was pulsed repetitively with a period of 50 ms. Within each pulsing cycle, two current steps are employed in succession. An initial, low-current step produces the narrow emission line one ordinarily associates with hollow cathodes. However, during that low-current step, a population of atoms is built up at the front of the hollow cathode itself, to exaggerate the self reversal produced in the succeeding high-current pulse. For reasons stated above, this high-current pulse must be relatively short; a value of 0.3 ms was chosen for the present study. Following the high-current pulse, lamp current is reduced to an "idling" level (1 ma) for 40 ms until the next current cycle. Because of the relatively low duty factor of this current waveform, hollow-cathode lamps operated in this new mode are actually sustained at a lower

average current than during conventional usage, so that lamp lifetime is not appreciably shortened.

Because of the differing volatilities and broadening characteristics of various elements, the values of the low-current step and high-current pulse in the waveform of Fig. 6 are individually selected for each element. Values of these currents are compiled in Table I. Understandably, a compromise between the extent of broadening and lamp lifetime was selected as a criterion for adopting particular current levels. For a figure-of-merit to indicate line broadening, a parameter termed "modulation depth" was defined as the ratio of the slopes of working curves obtained with the new background-correction method and with conventional low-current operation. That is, modulation depth could be calculated from the working curves of Fig. 5 as the ratio of the difference in slopes of the two curves ("delta") to that of the curve labeled "low current". For the 30 elements most commonly determined by atomic absorption spectroscopy, the mean modulation depth was found to be 53%, with a standard deviation of 21%. Overall, the modulation depths ranged from a low of 16% (Hg) to a high of 87% (Cd). Modulation depths for individual elements are listed in Table I along with measured lamp lifetimes. In Table I, it is important to note that some lamps have not yet been tested to failure; for these lamps, minimum lifetime values are cited.

Using the current values listed in Table I, working curves were obtained for several elements in an air-acetylene flame. Three of these curves, for Pb, Cu, and Ni, are reproduced in Fig. 7 and show the shape of the "delta" curve produced by the new

background-correction system. Importantly, this curvature is only slightly greater than that exhibited by a conventional single-beam hollow-cathode measurement and can easily be employed for routine determinations with the computer-monitored system used here.

The ability of the new technique to correct for scattering, molecular absorption, and atomic line interference was evaluated. As a severe test, 5 ppb cadmium in a synthetic sea-water sample (2% NaCl) was first examined. When sea water is determined using electrothermal atomization atomic absorption, the high salt matrix produces a great deal of particulate and molecular "smoke" during the atomization step, which then attenuates source radiation and renders the determination of individual elements very difficult. Cadmium is particularly susceptible to this interference. In Fig. 8, the ability of the new system to overcome this interference is dramatically apparent. In Fig. 8, the larger curve, reaching a peak absorbance of nearly 3, shows the uncorrected atomic absorption response to 10 uL of the sea-water sample; the small bump on the leading edge of the curve represents the cadmium component. Under background-correction conditions, the much smaller curve in Figure 8 was generated, indicating relative freedom from interference. As a further test, a real sea-water sample (obtained from the Virginia Institute for Marine Science) was examined. Manganese, like cadmium, suffers greatly from background interference during the electrothermal atomization of sea water and produces curves similar to those in Fig. 8. Nonetheless, background correction

with the new method yielded a value for manganese in the sample of 2.1 ± 0.1 ng/ml, in close agreement with the specified VHS value of 2.0 ± 0.1 ng/ml.

The new technique is able to correct even for atomic-absorption spectral-line overlap in some cases. Of course, direct spectral-line overlap is rare in atomic absorption because of the monochromaticity of the hollow-cathode primary source. However, some cases of such interference do exist and a notorious one is the influence of the nickel spectrum on the nearby line of antimony at 231.15 nm. Despite the proximity of these lines, the new background-correction technique is able to overcome their interference, because of the small and controllable degree of spectral-line broadening which occurs in the high-current pulse mode. To test this ability, a 2% nickel solution was examined with an antimony hollow-cathode lamp. Because the sample contained no antimony, there should ideally be no absorption by the nickel solution. However, absorbance-time curves obtained with an electrothermal atomizer, shown in Fig. 9, show the degree of interference in an uncorrected instrument. As expected, the extremely broad spectral window utilized by the deuterium arc method for background correction is unable to overcome this interference, as also apparent from Fig. 9. In contrast, the new background-correction approach (immodestly labeled S-H after the authors names) registers a complete absence of interference.

Of course, to obtain the degree of freedom from interference illustrated in Fig. 9 required a careful adjustment of the degree of broadening of the hollow-cathode-lamp line width. However, such adjustment is relatively simple with the new S-H technique

and under continuous atomization conditions can be effected simply. One need only atomize continuously the interferent and adjust lamp current during the high-pulse cycle until the effect of the interferent disappears. Because of the rarity of such interferences, it is appropriate to employ this adjusted high-pulse current routinely.

The ability of the new S-H method to overcome background interferences in real samples was tested further by the determination of selenium in two standard reference nickel alloys. The results of that analysis are compiled in Table II, where the agreement between the background-corrected AA results and those obtained by neutron activation analysis is apparent.

Because the S-H method for background correction necessarily yields a lower working-curve slope than would a single low-current hollow-cathode lamp (cf., Fig. 5), it is important to compare the detection limits which the new system yields with those available from competitive approaches. This comparison is made in Table III. Not surprisingly, because background correction techniques utilize the difference in a pair of measurements, the new method for background correction yields detection limits which are slightly poorer than those obtained under conditions where no background correction is employed. However, detection limits with the new technique are comparable to those produced by competitive approaches.

In summary, a new method for background correction has been developed which combines many of the advantages of competitive techniques. Like the Zeeman approach, it requires only a single

source and single-beam optics so that alignment is simplified. Moreover, the background correction is made very near the analytical wavelength, so that sloping backgrounds caused by molecular absorption should not pose significant problems. Also, background correction is made very rapidly so that fluctuating backgrounds can be followed, even for rapid atomizers such as carbon or tantalum furnaces. However, unlike the Zeeman scheme, the new method requires no special instrumentation and is usable at all resonant wavelengths with existing sources.

ACKNOWLEDGEMENT

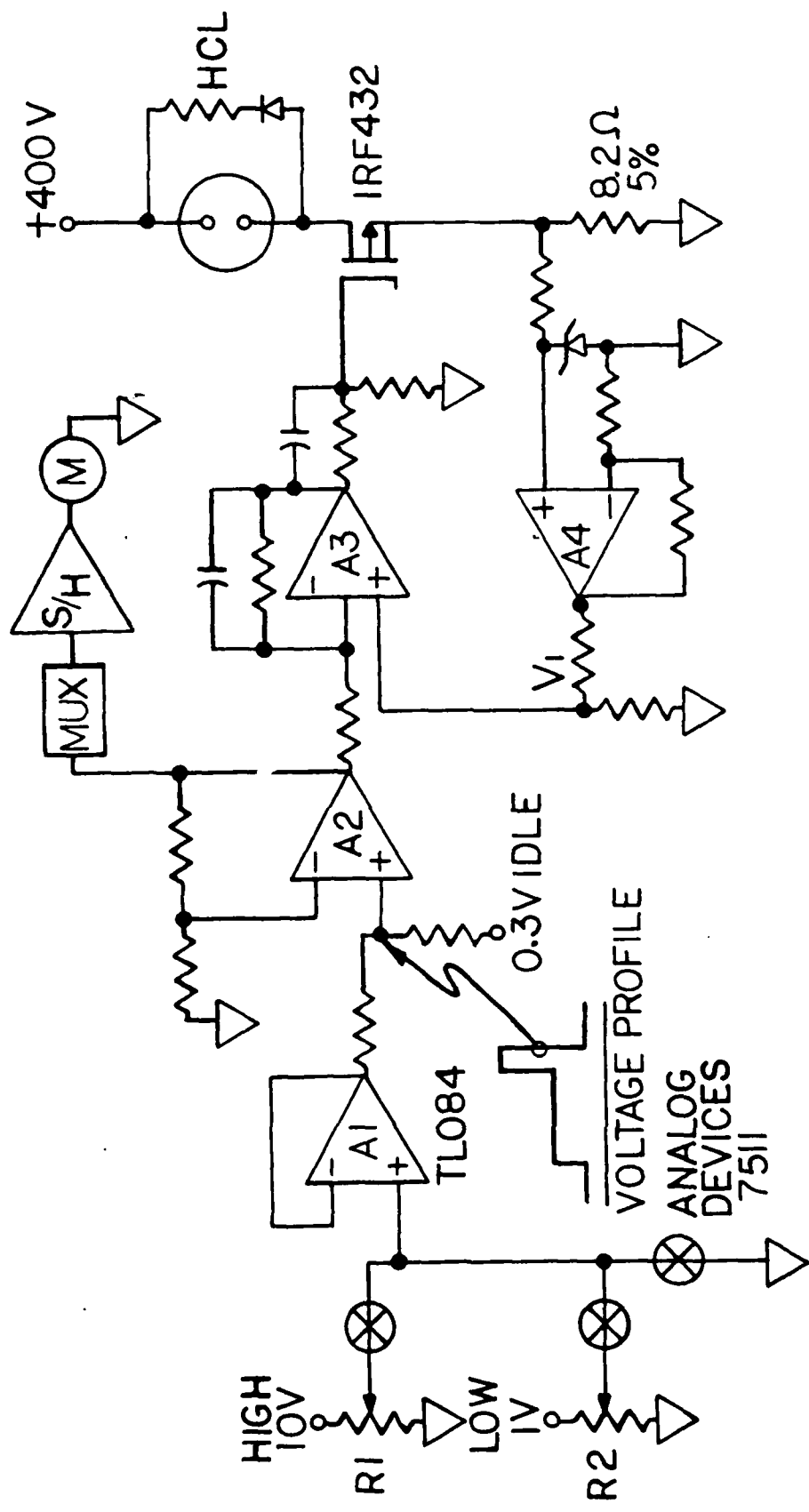
Supported in part by the Office of Naval Research and by the National Science Foundation. We greatly appreciate the invaluable technical assistance and suggestions provided by D. Pfeil, R. Langellotti, R. Schleicher and R. Savage.

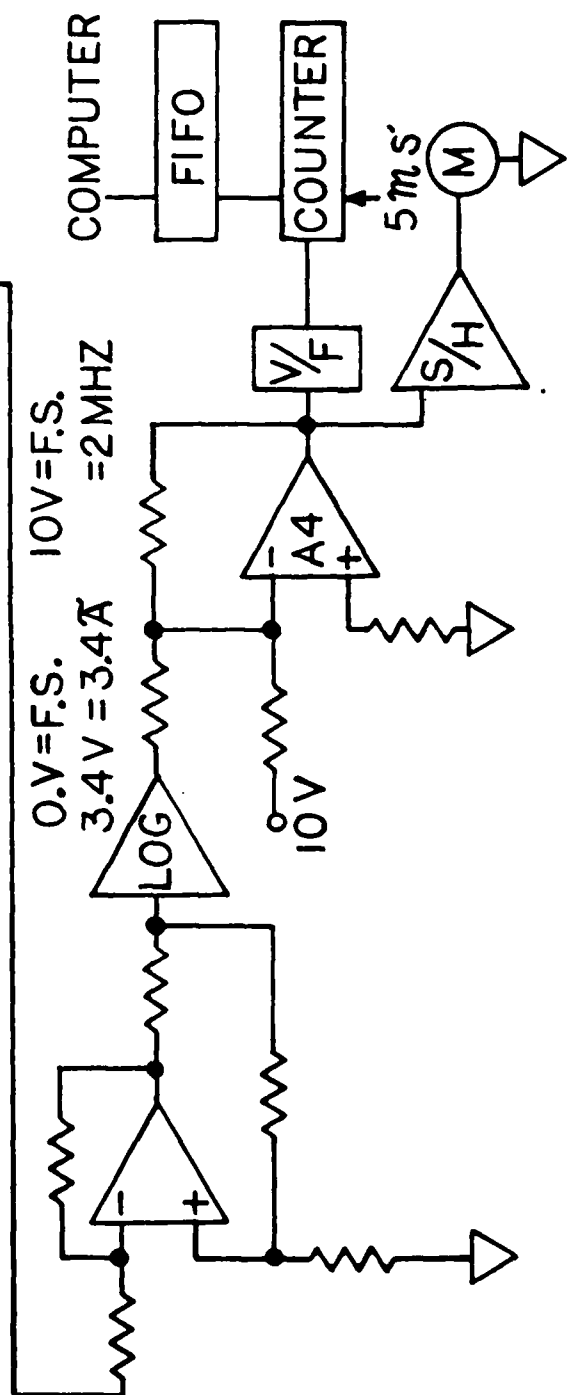
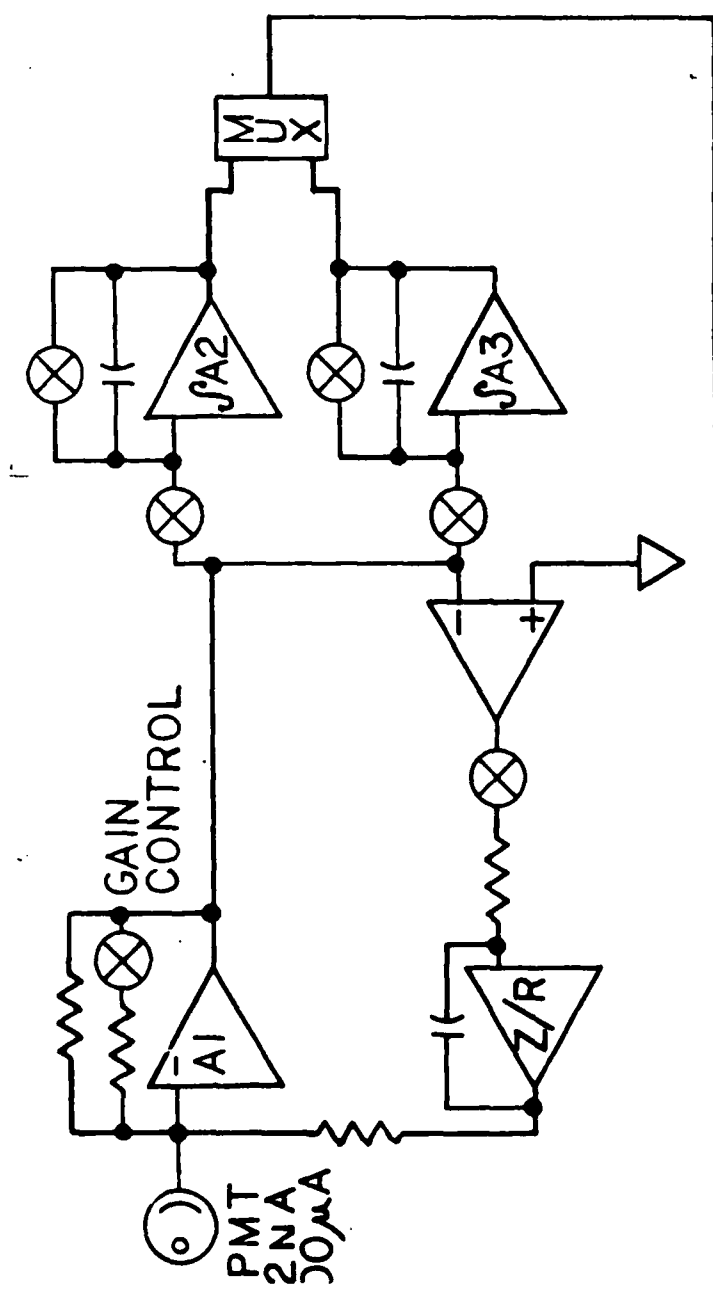
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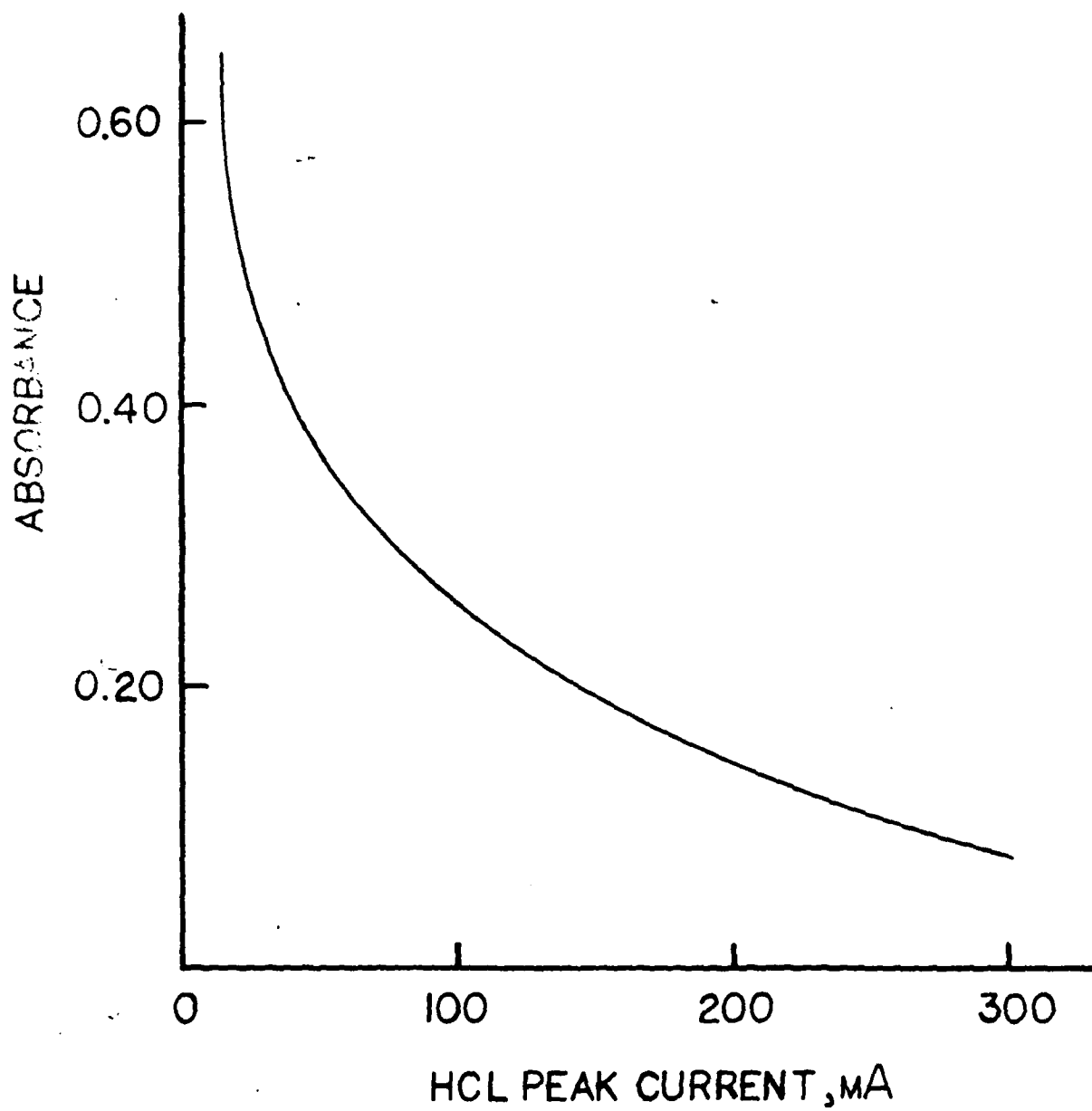
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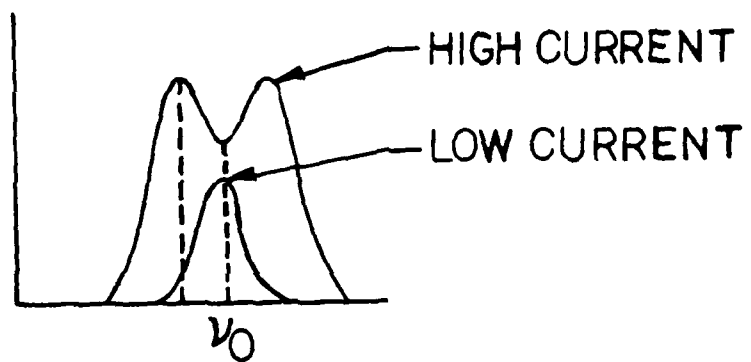
Figure Captions

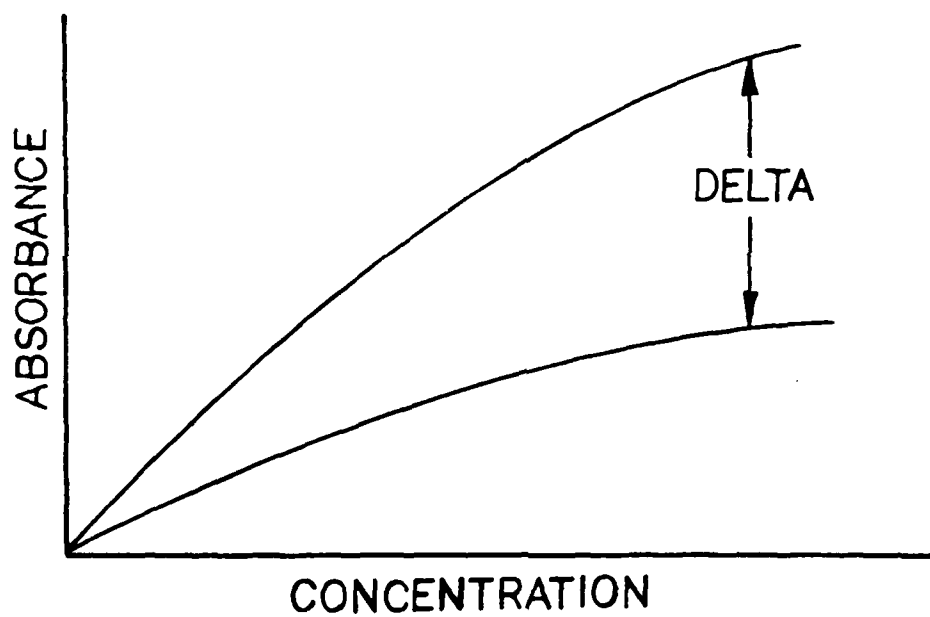
- Fig. 1. Schematic diagram of electronic drive circuit for controlled hollow-cathode lamp current. See text for discussion.
- Fig. 2. Schematic diagram of readout system for detecting and digitizing signals from new background-correction apparatus. See text for discussion.
- Fig. 3. Effect of hollow-cathode lamp operating current on the apparent absorbance of Cd ($1\text{ }\mu\text{g/mL}$) aspirated into an air-acetylene flame.
- Fig. 4. Stylized portrayal of hollow-cathode-lamp line profiles generated under low-current and high-current operation.
- Fig. 5. Working curves for Ni in a $\text{N}_2\text{O-C}_2\text{H}_2$ flame obtained under conditions of high- and low-current operation of a hollow-cathode lamp. Difference between curves, labeled "delta", is used for background correction. See text for discussion.
- Fig. 6. Current waveform used to drive the hollow-cathode lamp in the new background-correction device. The time between low-current and high-current segments (t) is only 4.5 ms, indicating the temporal proximity of background correction.
- Fig. 7. Background-corrected working curves for Cu, Ni, and Pb obtained with new device.
- Fig. 8. Atomization curves for 50pg Cd in 200 μg NaCl matrix, obtained with a carbon furnace. The larger curve (1) shows the strong response to the salt matrix obtained when no background correction is employed. The use of the new background-correction technique reveals the true temporal profile of Cd atomization (curve 2).
- Fig. 9. Electrothermal atomization of a 2% Ni solution shows the ability of the new device to correct interference even from spectral-line overlap. A selenium hollow-cathode lamp, operated in the conventional mode (upper curve) shows strong interference from Ni absorption. A deuterium background corrector overcomes only partially this interference (middle curve). However, the new S-H method exhibits freedom from the interference (lower curve).

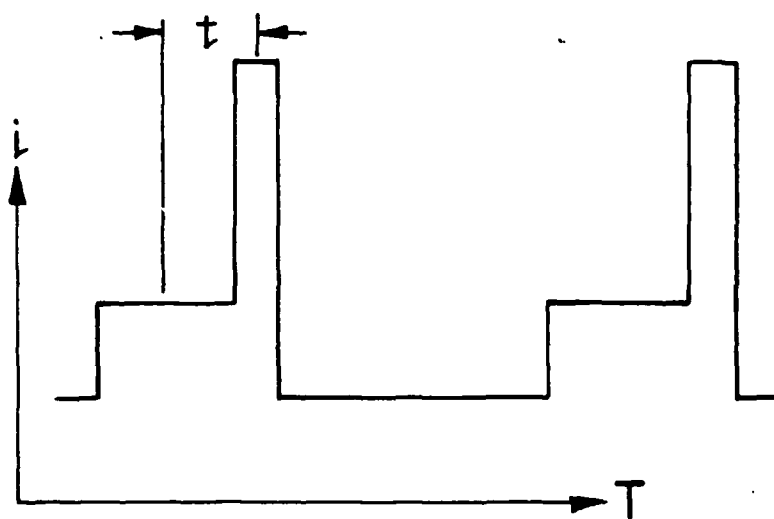


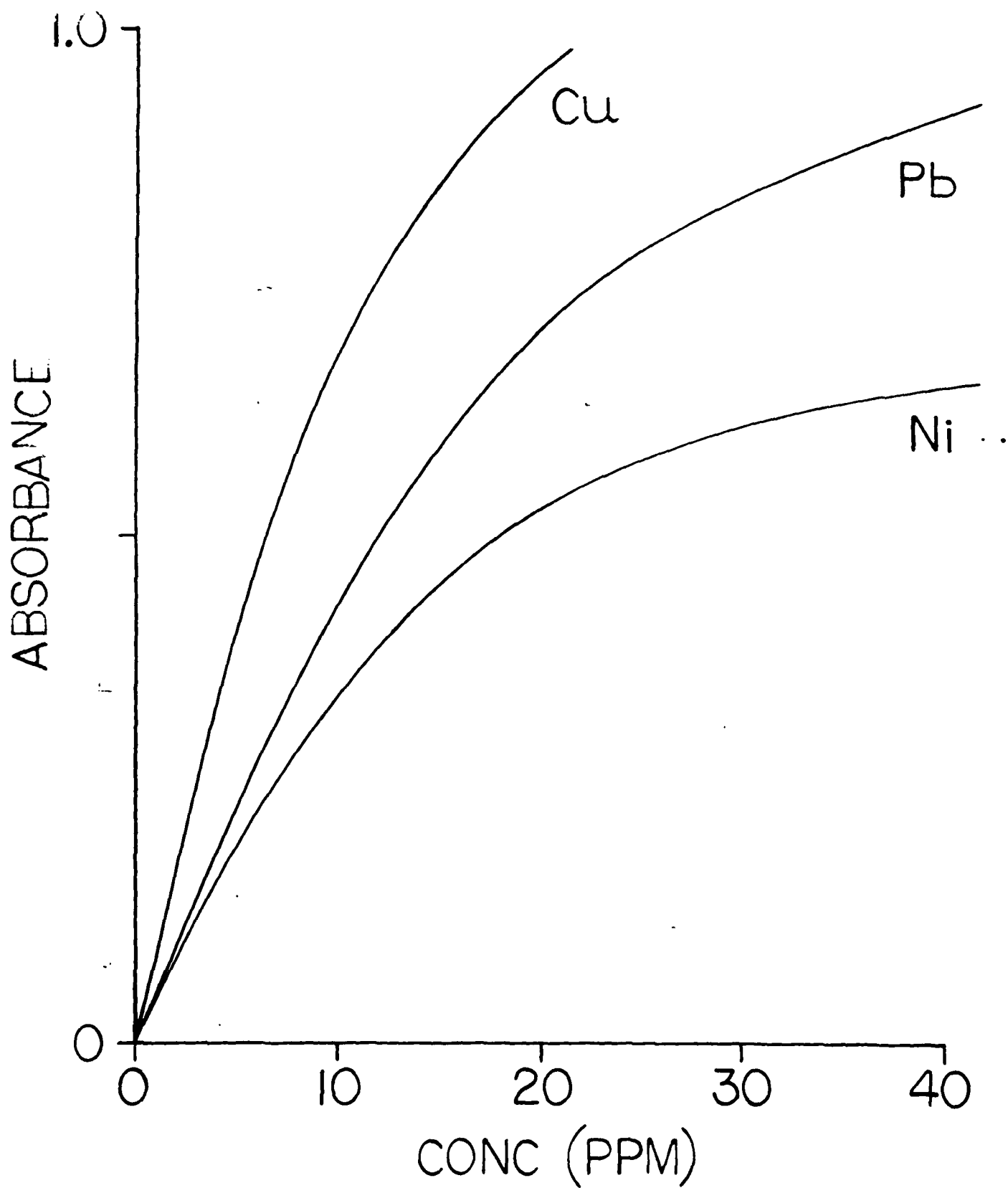


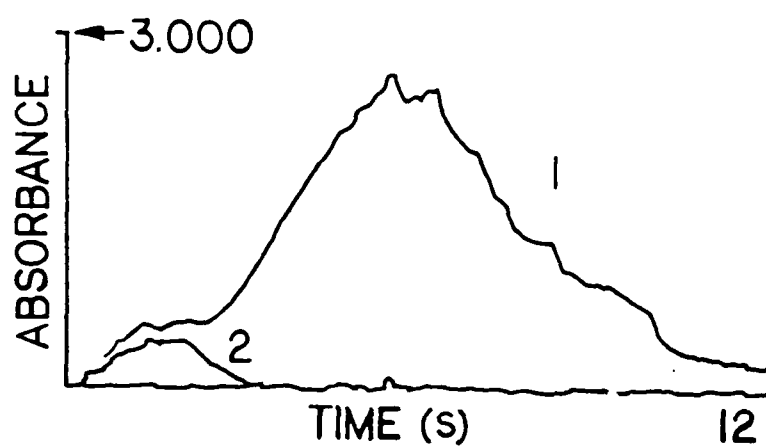












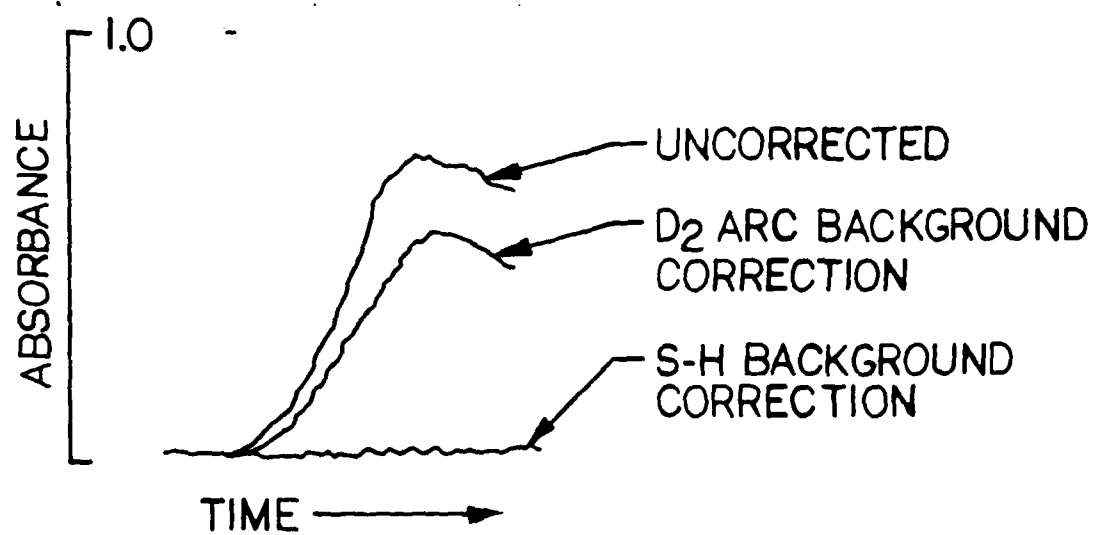


Table I. Modulation Depth and Hollow-Cathode Lamp
Lifetimes Obtained for Elements Frequently
Determined by Atomic Absorption Spectrometry

Element	Low-Current Step (mA)	High-Current Pulse (mA)	Modulation Depth (%)	Lamp Lifetime (mA-hrs)
Ag	8	200	82	a
Al	26	400	20	a
As	18	300	41	a
Au	12	200	38	a
Ba	24	300	22	4900
Cd	8	200	87	a
Co	14	300	59	a
Cr	16	400	42	a
Cu	10	300	62	a
Fe	12	300	43	4500
Hg	27	300	16	a
Mg	6	300	74	a
Mn	8	300	63	a
Ni	8	300	65	4536
Pb	8	250	59	3300
Se	25	300	57	a
Sn	8	300	41	a
V	20	400	19	a
Zn	8	300	91	a

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Table II. Determination of Se in NBS Standard Reference
Material Nickel Alloys Using New S-H Background-
Correction Method

<u>Alloy</u>	NBS Certificate <u>(Neutron Activation Method)</u>	Furnace AA <u>(S-H System)</u>
SRM 897	9.1 $\pm$ 0.1	9.7 $\pm$ 1.6
SRM 898	2.00 $\pm$ 0.02	1.5 $\pm$ 0.7

Table III. Flame AA Detection Limits ($\mu\text{g/mL}$)

<u>Element</u>	<u>No Background Correction</u>	<u>D₂ Arc Correction</u>	<u>S-H Method</u>
Ag	0.002	0.004	0.004
Al	0.02	0.04	0.1
As	0.1	0.1	0.3
Au	0.01	0.02	0.01
Be	0.001	0.002	0.001
Cd	0.001	0.002	0.002
Co	0.005	0.01	0.01
Cu	0.002	0.004	0.005
Cr	0.003	0.006	0.007
Fe	0.005	0.01	0.01
Mn	0.003	0.006	0.005
Ni	0.008	0.02	0.008
Pb	0.02	0.04	0.04
Pt	0.05	0.1	0.2
Se	0.1	0.1	0.2
Sn	0.08	0.2	0.2
Zn	0.006	0.002	0.001

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