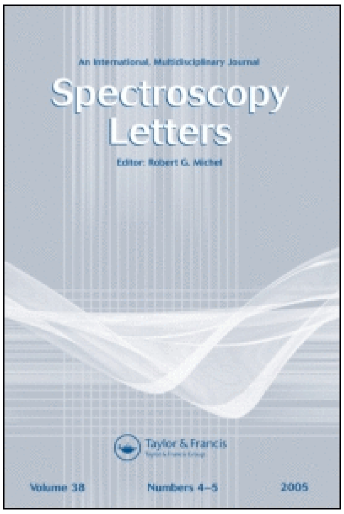

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SIMULTANEOUS MULTIELEMENT QUANTITATIVE SPECTROCHEMICAL ANALYSIS USING A DC ARC SOURCE AND A COMPUTER COUPLED PHOTODIODE ARRAY SPECTROMETER

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Self scanning linear arrays of silicon photodiodes have been utilized as multichannel detectors in a variety of spectrochemical measurements (1,2,3,4). These arrays have densities of 1000 photodiodes per inch and can be thought of as completely solid state single line image sensors. In some earlier work (3) a spectrometer based on this detector was utilized for qualitative dc arc spectrochemical analysis. In this note we report on the utilization of an improved computer coupled photodiode array spectrometer system for simultaneous multielement quantitative analysis with a dc arc source.

A block diagram of the computer coupled photodiode array spectrometer is shown in Fig. 1. The basic characteristics and operation of the photodiode array have been previously discussed in the literature (1). The particular array

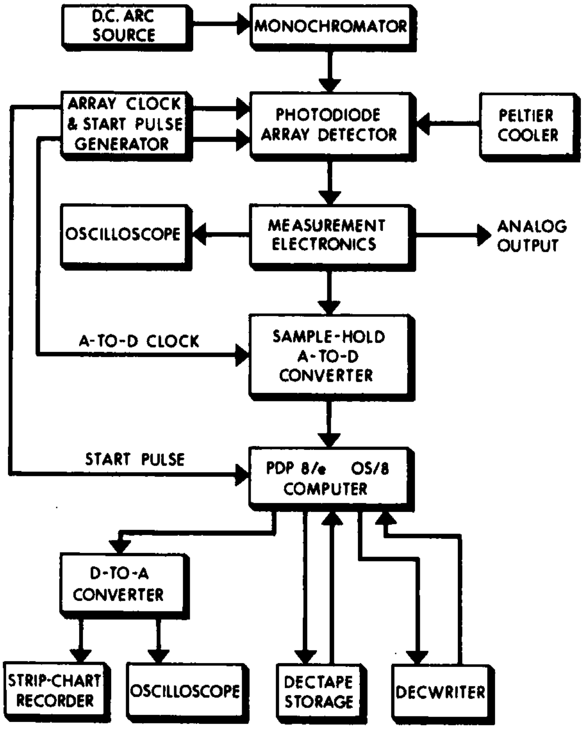

FIG. 1

Block diagram of computer coupled photodiode array spectrometer.

used in this study consisted of a linear array of 512 photodiodes and was 0.512" long. The array was clocked at 50 kHz and the time between start pulses (the integration time) was 2 sec. In order to use an integration time this long the array was cooled to ∿-10°C with a Peltier cooler to minimize dark current.

The 512 element array was mounted in the exit focal plane of a Heath monochromator (EU-700) and ∿270 Å of spectrum could be simultaneously measured. An ARL arc stand was positioned in front of the entrance slit of the monochromator with the analytical gap about 20 cm from the slit. No coupling optics were used. The samples were arced using a Jarrell Ash 43100 Utility DC-Arc at a current of 13 amps. The Cu samples were arced in Ultra Carbon 118 cups with 1688 upper electrodes and the brass samples in National 4006 cups with 3951 upper electrodes. All samples were made up from pure metal powders or oxides.

The photodiode array is an almost ideal detector for digital acquisition of spectra as the array samples the wavelength axis by its presence in the exit focal plane of the monochromator. The digitizing system consists of a sample and hold module with a 50 nsec aperture time (Analogic MP 250) coupled to a 10 bit ADC with a conversion time of 10 μsec (Analogic M 2810). After conversion the sample is stored in the computer which is a PDP 8/e with a DECtape based OS/8 operating system.

The data acquisition is sequenced by the same start and clock signals which sequence the scanning of the array. The array start pulse initiates the acquisition of a single scan of spectral information which, for a 512 point scan, is acquired in 10 msec (50 kHz clock rate). One scan is taken every 2 sec, which is the time between start pulses (integration time), and any preselected number of scans can be time averaged in the computer. Little random noise is present on the signals but time averaging is quite useful in reducing quantizing noise (5). The final spectrum can be displayed on an oscilloscope or a strip chart recorder via a DAC, listed on the DECwriter terminal or permanently stored on magnetic tape (DECtape) for further processing.

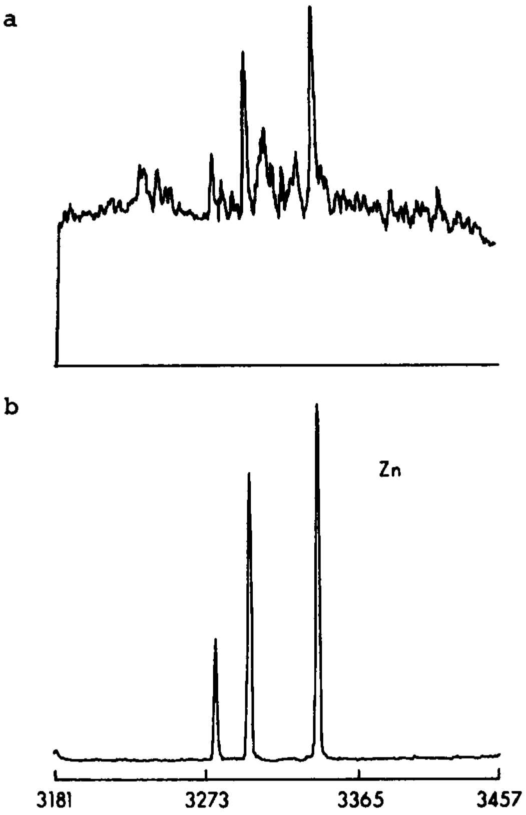

FIG. 2

a) Zn spectrum plus dark current and fixed pattern noise
b) Zn spectrum after subtraction of background.

The data acquisition program is written in a combination of FORTRAN and SABR languages.

Even though the array is cooled a significant dark current level is still present as well as a fixed pattern noise component. After termination of the arc an equal number of background scans are subtracted from the acquired spectrum in order to remove the dark current and fixed pattern noise components. The importance of being able to subtract these is shown in Fig. 2. A Zn spectrum (3181-3457 Å) superimposed

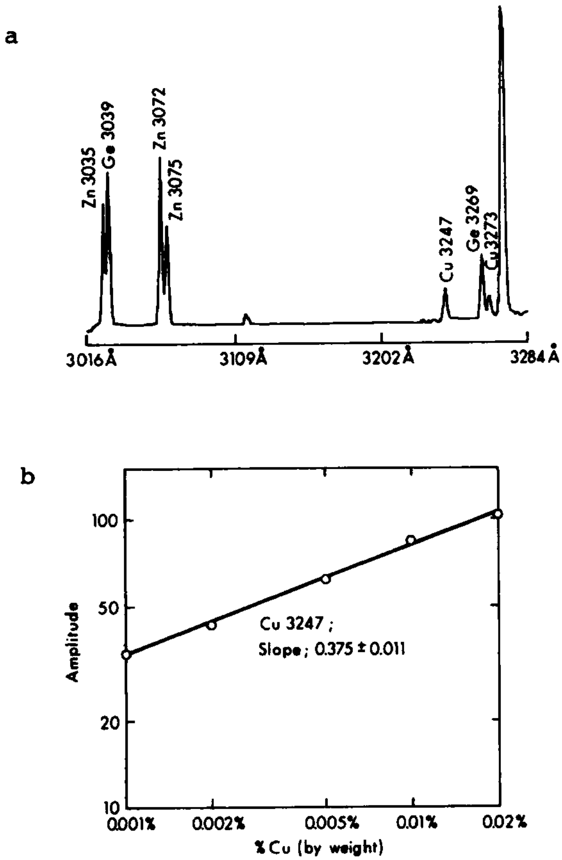

FIG. 3

a) 0.001% Cu in ZnO matrix
b) Analytical curve for Cu 3247 in ZnO matrix

on the dark current and fixed pattern noise of the array is shown in Fig. 2a. The spectrum resulting when these components are subtracted out is shown in Fig. 2b.

As a simple test for the system an analytical curve for Cu in a ZnO matrix was measured. The spectrum of a sample containing 0.001% Cu in a ZnO matrix is shown in Fig. 3a. Eight scans were time averaged resulting in a total measurement time of 16 sec. An internal standard of GeO_2 (1%) was

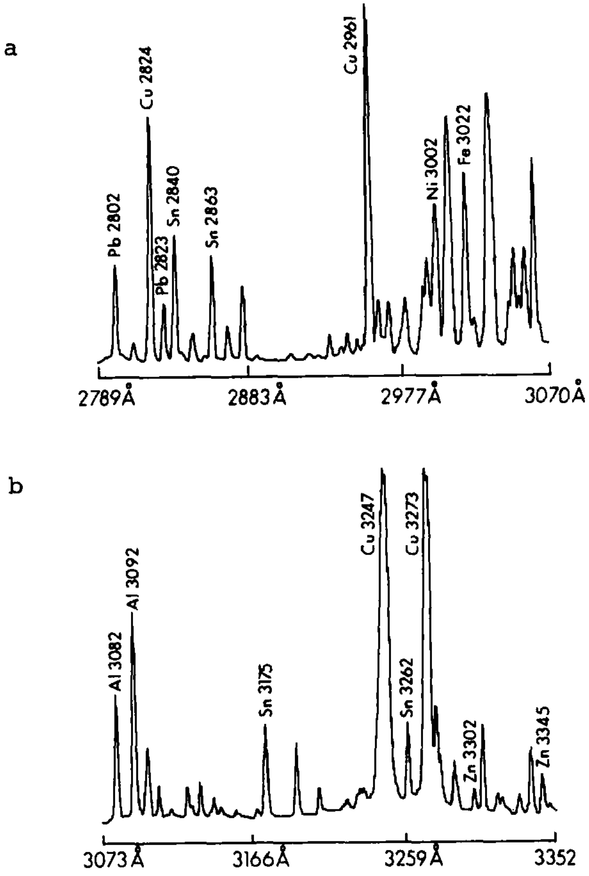

FIG. 4

Spectra of brass sample.

added to the samples but it was found that an analytical curve could be established without the use of an internal standard. The analytical curve obtained by directly plotting the intensity of the Cu 3247 Å line (corrected for background) as a function of concentration is shown in Fig. 3b. This line is quite susceptible to self absorption and this would account for the small slope which, in the ideal case, should be unity.

The simultaneous measurement of a number of analytical curves for several elements in a synthetic brass sample was

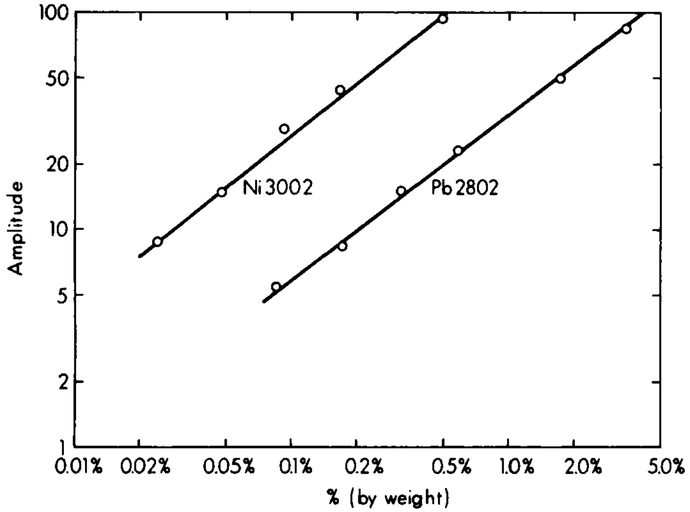

FIG. 5

Analytical curves for Ni 3002 and Pb 2802.

also carried out. It was necessary to measure two spectral regions in order to obtain useful lines for all elements. The spectrum of a sample containing 2.1% Zn, 1.7% Pb, 2.0% Sn, 0.5% Ni, 0.55% Fe, 1.18% Al and 92% Cu is shown in Fig. 4a for the 2789 to 3070 Å region and in Fig. 4b for the 3073 to 3352 Å region. Fifteen scans were time averaged resulting in a total measurement time of 30 sec. The lower spectral region (Fig. 4a) was used for the simultaneous measurement of Pb, Sn, Ni, and Fe and the upper spectral region (Fig. 4b) for Al, Sn, and Zn. Again analytical curves were established without using an internal standard. Two typical analytical curves are shown in Fig. 5 for Ni and Pb. The slopes of the log-log plots as determined by linear least square fits for all the analytical lines chosen are listed in Table 1. In most cases the slopes are not unity indicating the presence of self absorption which is not unexpected at the concentration ranges of these elements.

These results indicate that the computer coupled photodiode array spectrometer should be quite useful for quantitative spectrochemical analysis with a dc arc source. In particular the multichannel nature of the detector, the ease of digitizing spectra, and the establishment of analytical curves without using an internal standard are all assets of the system. In addition, spectra representing sequencial time integrated segments of a total arc burn could readily be acquired and stored in the computer. Such time studies are important during the development and implementation of most dc arc spectrochemical analyses. Work is now in progress on completely automating the time study of a sample with this system.

TABLE 1

Analytical Curve Data for Brass Samples

Elemental line	Concentration range (%)	log-log slope
Pb 2802	.09 - 3.5	0.747 ± 0.015
2833		0.516 ± 0.010
Sn 2840	.1 - 2.0	0.700 ± 0.023
2863		0.802 ± 0.039
Ni 3002	.02 - .50	0.793 ± 0.035
Fe 3022	.05 - .18	1.029 ± 0.022
Al 3082	.12 - 2.4	0.652 ± 0.043
3092		0.580 ± 0.031
Sn 3174	.10 - .68	0.869 ± 0.048
3262	.20 - 4.0	0.955 ± 0.028
Zn 3303	.1 - 2.1	0.946 ± 0.042
3345	.2 - 4.2	1.081 ± 0.037

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