

## Exploding wire excitation for trace analysis of Hg, Cd, Pb and Ni using electrodeposition for preconcentration

J. A. HOLCOMBE and R. D. SACKS\*

Department of Chemistry, University of Michigan, Ann Arbor,  
Michigan 48104, U.S.A.

(Received 16 March 1973; in revise form 30 July 1973)

**Abstract**—The use of exploding silver wires for spectrochemical excitation is described. The apparatus used in these studies is discussed along with the electrical and radiative properties of exploding silver wires. The use of controlled-potential electrodeposition onto silver wires for sample introduction is considered. Experimental parameters for electrodeposition and exploding-wire excitation are presented. Cd, Ni, Hg and Pb are considered for analysis and show absolute detection limits of 10 ng, 10 ng, 30 ng and 15 ng, respectively. These amounts of material on the wire represent relative detection limits of 0.001 ppm, 0.002 ppm, 0.003 ppm and 0.001 ppm respectively in the analytical solutions. The exploding wire excitation method exhibits minimal matrix dependency and good reproducibility. Percent relative standard deviations for Cd, Ni, Hg and Pb are  $\pm 17.3\%$ ,  $\pm 16.6\%$ ,  $\pm 26.5\%$  and  $\pm 12.4\%$ , respectively. Sample introduction by controlled-potential electrodeposition offers not only a convenient means of preconcentrating trace metals from solution but also the possibility of selectively plating one element in the presence of a large excess of other elements in solution.

### INTRODUCTION

IF ELECTRICAL energy is delivered to a conductor at a rate which exceeds its dissipation ability, ohmic heating results. If the energy available is sufficiently large, melting and vaporization will occur. Under controlled, laboratory conditions, the energy delivery rate can be great enough to cause explosive vaporization of the conductor. Accompanying this explosion is a loud report and an intense flash of light. The explosion is achieved generally by a direct capacitive discharge through the conductor. Capacitance values in the range from a fraction of a  $\mu\text{F}$  to several hundred  $\mu\text{F}$  commonly are used with storage voltages varying from a few kV to several hundred kV. Currents in excess of 50 kA are common. In most work the residual inductance and resistance in the circuit are kept at a minimum to maximize both the energy delivery rate and the fraction of available energy dissipated in the wire.

The first exploding wire study was reported by NAIRNE [1] in 1773. He used the energy stored in 64 Leyden jars to explode a thin iron wire. The modern period of investigations into the exploding wire phenomena began in 1920 with the spectroscopic work of ANDERSON [2]. Other significant studies about this time also were conducted by ANDERSON and SMITH [3, 4]. Since these initial studies, interest in

---

\* To whom correspondence should be directed.

[1] E. NAIRNE, *Proc. Roy. Soc.*, London (Dec. 1773).

[2] J. A. ANDERSON, *Astrophys. J.*, **51**, 37 (1920).

[3] J. A. ANDERSON and S. SMITH, *ibid.*, **64**, 295 (1926).

[4] S. SMITH, *ibid.*, **61**, 186 (1925).

this phenomena has increased steadily. A series of four conferences dealing specifically with studies related to the exploding wire phenomena was held between 1959 and 1967 [5-8].

Most of the work conducted to date is concerned with the physical aspects of the discharge and has little direct application to analytical spectroscopy. In 1966, GOODFRIEND *et al.* [9] noted the large number of iron emission lines in the spectrum resulting from the explosion of a boron filament containing a few ppm iron. More recently SACKS and HOLCOMBE [10, 11] reported the direct application of the exploding wire to spectrochemical analysis. They considered the spectroscopic effects of varying the explosion parameters using Cu and Ag wires. This paper examines the feasibility of the exploding wire as an excitation source for quantitative emission spectrochemical analysis.

Controlled-potential electrodeposition is used to introduce the metal sample onto silver wires. Electrodeposition has been used from time to time as a preconcentration technique prior to neutron activation analysis [12], spark source mass spectrometry [13, 14] flameless atomic absorption spectrometry [15, 16], and r.f. plasma torch spectrometry [17]. For the most part, workers have used deposition at constant current and have not exploited the selectivity of potential control to separate interfering elements. Recently, however, controlled-potential deposition on metal foils prior to elemental analysis by ESCA was reported [18].

This paper will outline the equipment used in this study of the exploding wire, the experimental techniques involved in sample introduction, and finally, a discussion of the results obtained using this excitation source for quantitative spectrochemical analysis of solutions containing Pb, Hg, Cd and Ni.

### *Description of apparatus*

A block diagram of the exploding wire apparatus used in this study is shown in Fig. 1. Since the basic explosion circuit is an RCL tank, the ringing frequency will, in part, determine the rate at which energy is delivered to the wire from the capacitor

- 
- [5] *Exploding Wires*, Vol. 1, (W. G. CHACE and H. K. MOORE, eds.). Plenum Press, New York (1959).
- [6] *Ibid.*, Vol. 2 (1962).
- [7] *Ibid.*, Vol. 3 (1964).
- [8] *Ibid.*, Vol. 4 (1968).
- [9] P. L. GOODFRIEND, H. P. WOODS and L. J. PARCELL, *Anal. Chem.*, **38**, 1433 (1966).
- [10] R. D. SACKS and J. A. HOLCOMBE, "Exploding Wire Excitation for Spectrochemical Analysis," presented at the 11th National Meeting of the Society for Applied Spectroscopy, Sept. 10-15, 1972, Dallas, Texas.
- [11] J. A. HOLCOMBE and R. D. SACKS, "Exploding Wire Initiated Electrical Discharge Excitation for Spectrochemical Analysis," presented at the 20th Annual ANACHEM Conference, Oct. 9-11, 1972, Dearborn, Michigan.
- [12] H. B. MARK and F. J. BERLANDI, *Anal. Chem.*, **36**, 2062 (1964).
- [13] R. ALVEREZ, P. J. PAULSEN and D. E. KELLEHER, *Anal. Chem.*, **41**, 955 (1969).
- [14] P. J. PAULSEN, R. ALVEREZ and E. E. KELLEHER, *Spectrochim. Acta*, **24B**, 535 (1969).
- [15] H. BRANDENBERGER, *Chimia*, **22**, 449 (1968).
- [16] P. AHERTY and R. S. DORSETT, *Anal. Chem.*, **43**, 188 (1971).
- [17] R. WOODRUFF and D. SIEMER, *Appl. Spectry.*, **23**, 38 (1969).
- [18] J. S. BRINER and J. E. McCLURE, *Anal. Letters*, **5**, 737 (1972).

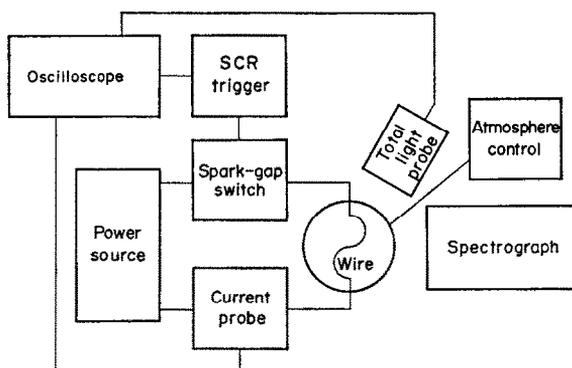


Fig. 1. Block diagram of exploding wire apparatus and various monitoring systems.

bank. This delivery rate needs to be sufficiently large to insure *explosive* vaporization of the wire. Because the requirements for a successful explosion and optimized energy transfer to the wire dictate the use of a relatively low inductance, low resistance source, all leads within the explosion circuit are kept short and are constructed of 3/8 in. dia copper tubing.

A schematic of the power supply is shown in Fig. 2. The discharge capacitor bank C consists of four General Electric Pyranol capacitors each rated at  $7.5 \mu\text{F}$  and 12.5 kV. A 12 kV, 30 mA neon-sign transformer  $T_2$  is used to charge one to four capacitors through a full-wave bridge rectifier and charging resistor  $R_C$ . The maximum energy capability of this system is 2160 J. The capacitors are discharged through the wire by means of a three-electrode, air-gap switch and the associated electronic triggering circuit shown in Fig. 3. In the triggering circuit a  $1.0 \mu\text{F}$  capacitor is charged to approximately 300 V. A 25 V signal from the gate output of a Tektronix 547 oscilloscope is fed into the cathode gate of the silicon control rectifier (SCR) thereby discharging the capacitor through the primary of an EG and G TR-69 pulse transformer. The secondary of the pulse transformer is directed to the three-electrode, air-gap switch to initiate its breakdown.

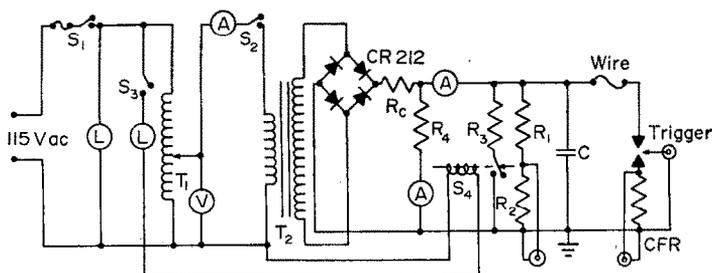


Fig. 2. Capacitive discharge excitation source.  $T_1$ : variable auto transformer;  $T_2$ : 0–12 kV high-voltage transformer;  $R_C$ : 500 k $\Omega$  charging resistor;  $S_4$  safety switch; C: Capacitor storage bank of 4–7.5  $\mu\text{F}$  Pyranol high-voltage capacitors; CFR: current following resistor for current waveform measurements; L: indicator lights; V: volt meter; A: ammeter; TRIGGER: 3 electrode spark-gap switch.

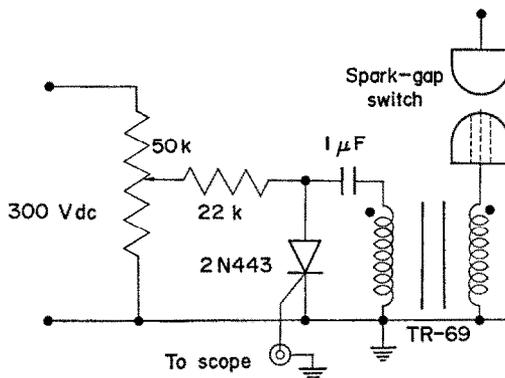


Fig. 3. Electronic triggering circuit. 25 mA signal applied to the SCR induces a high voltage spike from the secondary of the TR-69 pulse transformer.

The explosion chamber is shown in Fig. 4. The circular, copper electrodes used in holding the wire are required to maintain a uniform electric field so that symmetric expansion of the plasma can occur [19]. The electrode surfaces are hand buffed with steel wool prior to each explosion to prevent build up of any metal or dielectric layer on the electrodes.

The borosilicate glass chamber is 'O'-ring sealed to the upper and lower lucite base plates. Lucite spacers in the upper plate and rubber insulation around the

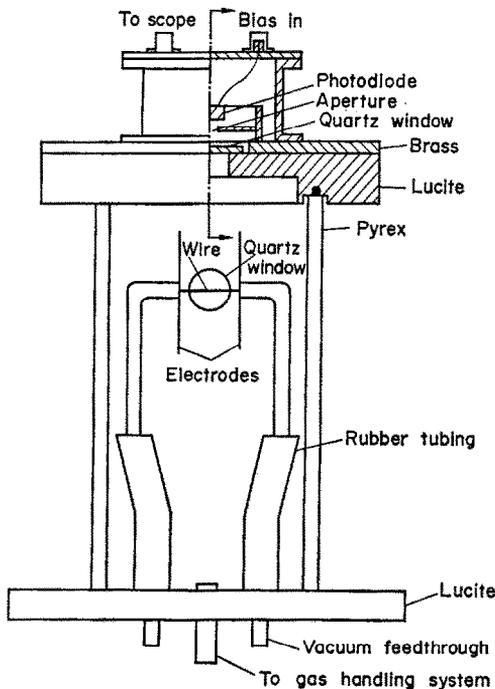


Fig. 4. Explosion chamber.

[19] H. BARTELS and J. BORTFELD, *Exploding Wires*, Vol. 3 (W. G. CHACE and H. K. MOORE, eds.). Plenum Press, New York (1964), p. 9.

bottom of the electrode arms are used to prevent occasional sparkover. A gas handling system provides control of the gas composition and pressure in the test chamber.

The explosion is viewed through a quartz window located on the side of the explosion chamber. A medium quartz Hilger spectrograph equipped with photographic detection is used to record the spectra.

An EG and G SA-100A high-speed photodiode in series with a 1 k $\Omega$  resistor and 94 V bias supply is used to monitor the light from the discharge within the spectral range from 3300–11,000 Å. The photodiode is housed above the top brass plate and placed behind a 1 mm dia light limiting aperture to prevent saturation during peak light emission.

The current probe (CFR in Fig. 2) is wired coaxially in series with the test wire and consists of a monel rod with a nominal resistance of 0.001  $\Omega$ . The output from both the current probe and the photodiode are monitored on the oscilloscope. Both of these monitoring systems are useful in electrical and plasma diagnostics.

### Electrical and spectral characteristics

Figures 5a and 5b show a typical oscilloscope trace of the current through the discharge and the photodiode response respectively when the initial energy stored on the capacitor is in excess of the thermodynamic amount required to vaporize the wire. The series of events during the explosion begins with ohmic heating of the solid followed by the solid-liquid transition and continued heating through the

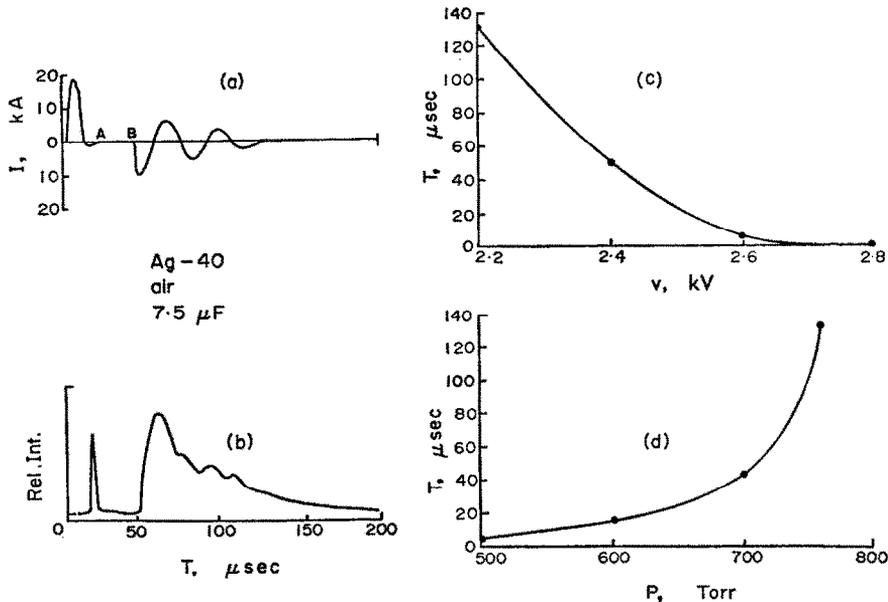


Fig. 5. (a) Discharge current waveform. Point A represents the start of the dwell period, and point B indicates the plasma restrike. (b) Photodiode response. (c) Effect of initial capacitor voltage on the length of the dwell period. (d) Effect of surrounding gas pressure on the length of the dwell period.

liquid phase. Once vaporization occurs, the presence of a dielectric vapor between the electrodes interrupts the current. This begins a dwell period of zero current as indicated by point A in Fig. 5a. At point B, the dwell ends with a plasma reignition through the vapor. Current now is carried by the metallic plasma and its waveform is that of a typical damped sine wave. A mechanism for restrike has been suggested by JÄGER and LOCHTE-HOLTGREVEN [20] and more recently considered by WITTIG and co-workers [21]. This mechanism agrees well with spectroscopic data obtained in this laboratory and will be discussed briefly.

The photodiode response after the restrike appears similar in form to that obtained from other high voltage discharges [22]. The unique feature of the trace is the light emission near point A just prior to the onset of the dwell period. The appearance of radiation prior to complete vaporization suggests that the wire is radiating as an incandescent solid or liquid.

The effects of initial capacitor voltage and gas pressure on the dwell period duration are shown in Figs. 5c and 5d respectively.

Time and spatially integrated spectra of the discharge exhibit two distinctive forms depending on the gas pressure surrounding the wire. Microdensitometer traces of two series of spectra which depict these two forms are shown in Figs. 6 and 7. Spectra for four different diameters of Ag wire ranging from A.W.G. 30

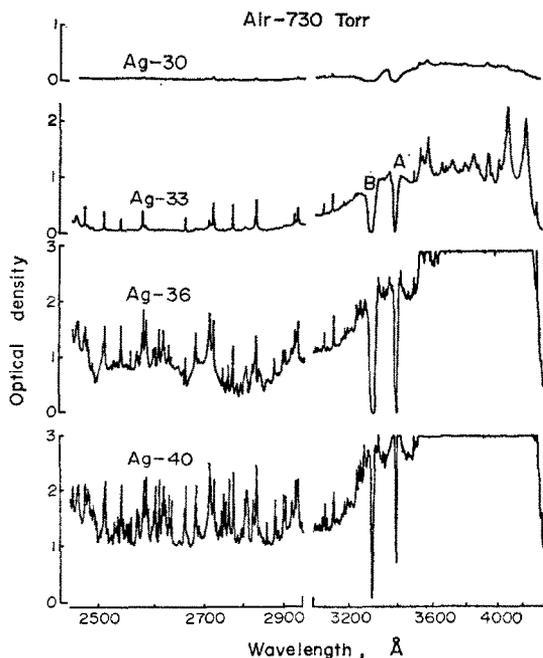


Fig. 6. Microdensitometer tracings of spectra resulting from explosions under atmospheric pressure conditions using Ag wire ranging in size from A.W.G. 30 to A.W.G. 40. Conditions for all explosions—5 kV, 7.5  $\mu$ F, 730 Torr in air.

[20] H. JÄGER and W. LOCHTE-HOLTGREVEN, *Exploding Wires*, Vol. 4 (W. G. CHACE and H. K. MOORE, eds.). Plenum Press, New York (1968), p. 41.

[21] S. L. WITTIG, R. A. ALTENKICH, E. P. PROBST, A. M. MELLOR, *Appl. Opt.*, **11**, 765 (1972).

[22] J. P. WALTERS, *Anal. Chem.*, **41**, 1540 (1968).

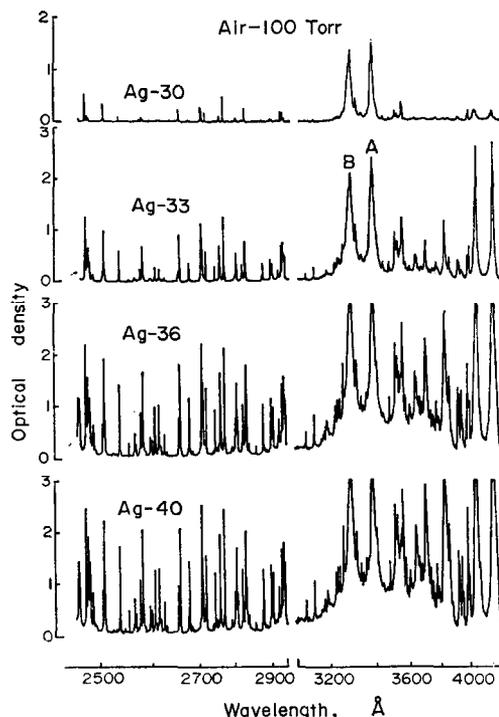


Fig. 7. Microdensitometer tracings of spectra resulting from explosions under low pressure conditions, i.e., 100 Torr in air. All other parameters identical with those cited in Fig. 6.

(0.25 mm dia) to A.W.G. 40 (0.078 mm dia) are shown in each Fig. All spectra were obtained in air using  $7.5 \mu\text{F}$  at 5 kV.

A significant difference between the wires exploded at 730 Torr and 100 Torr is the extreme self-absorption of the 3382 and 3280 Å Ag resonance lines, A and B, in the high pressure explosion while the same lines show no reversal at 100 Torr. The high pressure explosions also show significant broadening of all lines and an intense background continuum. It has been suggested [23] that the spectral differences in these two cases are the result of two differing restrike mechanisms. In the high pressure explosions current waveforms similar to that in Fig. 5a predominate. During the dwell period, the metal dielectric vapor continues to expand in a radial fashion, thereby creating a low pressure region in the center of the expanding cylinder. When this low pressure region satisfies the Paschen breakdown criteria [24], an axial restrike through the vapor core results. The axial restrike causes intense emission in the core. The high density, low temperature metallic vapor sheath surrounding the core results in an optically thick plasma with considerable self-absorption of resonance radiation.

[23] D. Y. CHENG, W. J. LOUBSKY and V. E. FOUSEKIS, *Phys. Fluids*, **14**, 2328 (1971).

[24] R. PAPOULAR, *Electrical Phenomena in Gases*. American Elsevier Publishing Co., Inc., New York (1965), p. 116.

Under low pressure conditions complete vaporization of the wire may not occur prior to restrike. Instead, current conduction is transferred directly, without a dwell, from the relatively high resistance molten wire to the low pressure metallic vapor sheath created by surface vaporization of the metal wire [20]. Figure 7 shows the results of such a peripheral restrike.

In considering explosion conditions for analysis, a low pressure gas appeared most attractive due to the presence of narrow emission lines, the lack of self-absorbed resonance lines, and the increase in signal to noise (S/N) ratio. However, as the pressure is lowered, the total light from the discharge decreases, and between 0.01 Torr and 10 Torr no radiation was detected under the reported experimental conditions. In addition, at pressures below about 10 Torr sampling of the electrode surfaces becomes appreciable. A pressure of 100 Torr provides a good compromise by providing an adequate S/N ratio, no detectable electrode sampling, and ample light intensity.

The spectral influence of air, Ar and He as a surrounding gas also was investigated. Time integrated spectra revealed no detectable radiation from any of these gases when used at a variety of pressures. However, a noticeable difference in the spectral features is apparent when comparing air and Ar with He. For any given pressure the background continuum of a Ag wire exploded in He is appreciably lower than a similar explosion in air or Ar. Spectra obtained in He at 100 Torr are shown in Fig. 8. These gas and pressure parametric investigations led to the choice of He

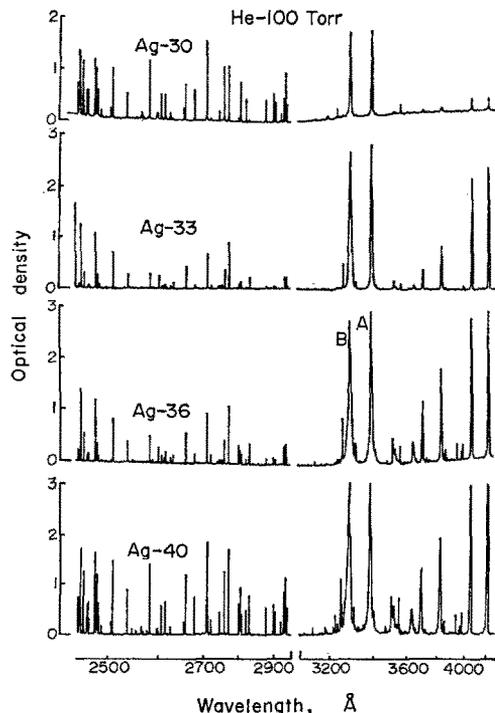


Fig. 8. Microdensitometer tracings of spectra resulting from explosions in 100 Torr of He. All other parameters, identical with those cited in Fig. 6.

at 100 Torr for analytical work. Further information is needed before any conclusive statements can be made concerning the strong dependence of the exploding wire emission on gas composition and pressure.

The 40 gauge Ag wire was chosen for analytical work since it showed greater intensity and reproducibility than the larger wires. The probable error in intensities of a Ag neutral atom and ion line for a series of six explosions of A.W.G. 40 wire is 5.8% and 4.7%, respectively. Instabilities in the plasma of larger diameter wire caused unpredictable motion relative to the detection system thus reducing reproducibility.

### EXPERIMENTAL PROCEDURE

The explosion conditions and source parameter used for analysis are given in Table 1. The Ag wire was obtained from Williams Gold Refining Company, Buffalo,

Table 1. Explosion conditions used for analysis

Initial capacitor voltage	5 kV
Storage capacitance	7.5 $\mu$ F
Residual source resistance	0.08 $\Omega$
Residual source inductance	2.8 $\mu$ H
Ringing frequency	34.8 kHz
Total stored energy	93.8 J
Wire support used	Ag -A.W.G. 40 (0.078 mm dia)
Length of wire exploded	35 mm
Mass of wire exploded	1.75 mg

New York, and has a nominal purity of 99.9%. The detection system used in the analyses consists of a Hilger medium quartz spectrograph with 10  $\mu$ m slit and Kodak SA-1 photographic plates developed in accordance with the manufacturer's specifications. The photographic plates are calibrated in the wavelength regions of interest using a 2-step rotating disc with an iron arc as a light source.

A three-electrode potentiostat was constructed for the electrodepositions. A conventional summing amplifier configuration using a Fairchild  $\mu$ A 741 operational amplifier, with complimentary emitter followers to provide higher output currents, was employed as the control amplifier with a National Semiconductor LM 302 voltage follower in the voltage measuring circuit. The potentiostat has an output of 100 mA at  $\pm 10$  V.

The plating cell is shown in Fig. 9. Three 4.5 in. wires are used in each deposition. Since the electrolysis is not exhaustive, stirring rate and cell geometry are carefully controlled to assure reproducible deposition. A Varian-Techtron model AA-5 atomic absorption spectrometer was used to analyze the plating solutions before and after electrodeposition to determine the percentage of material deposited in a 2-hr period. An acetylene-air flame was used for this analysis and conditions adjusted according to the manufacturer's manual specifications.

The 300 ml plating bath volume was 0.05 *M* in KCl supporting electrolyte and 0.001 *M* in  $\text{NH}_2\text{OH} \cdot \text{HCl}$ , which is used as an anodic depolarizer in the reduction of Pb(II) from solution. KCl was chosen as the supporting electrolyte because of the availability of documented sources for reduction potentials in this medium.

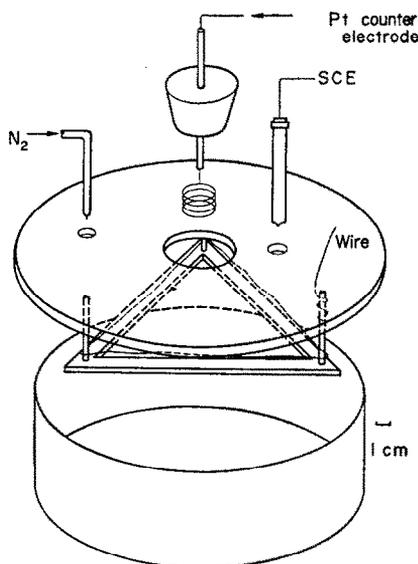


Fig. 9. Cell used for electrodeposition. A magnetic stir bar is used for solution agitation.

Reagent grade chemicals were used throughout to prepare stock solutions containing 0.1% by weight of the analyte. Other standard solutions were prepared by dilution. The presence of the analyte as an impurity either in the water used for dilution or in the electrolyte components was checked periodically by running a 2-hr electrolysis using the deposition cell containing electrolyte only. If the spectra resulting from the explosion of these wires displayed spectral lines not found in Ag wires which had not been subjected to the plating step, purification of the electrolyte by exhaustive electrolysis onto a Hg pool or Cu plate was performed.

Before deposition, the wires were rinsed in acetone and dilute  $\text{HNO}_3$  to remove surface oils and contaminants. Table 3 summarizes the experimental parameters

Table 2. Analytical conditions

	Cd	Ni	Hg	Pb
Boiling point ( $^{\circ}\text{C}$ )	765	2732	357	1744
Ionization pot. (V)	8.99	7.63	10.43	7.42
Electrodeposition potential vs. S.C.E. (V)	-1.10	-1.40	-0.30	-0.80
Plating efficiency (%) <sup>a</sup>	24	14	27	33
Analytical line or line pair ( $\text{\AA}$ )	Cd(I) 3466.20 Ag(I) 3542.61	Ni(II) 2510.87 Ag(II) 2504.08	Hg(I) 2536.52 Ag(I) 3542.61	Pb(I) 2833.07
Range of relative concentrations used in plating bath (ppm)	0.015-7.5	0.005-10	0.33-146	0.005-6.6

<sup>a</sup> The plating efficiency represents the percent of the material plated from the solution onto the Ag wires in a 2-hr period.

Table 3. Plating efficiency reproducibility

Hg		Pb	
Run	Fraction of material deposited <sup>a</sup>	Run	Fraction of material deposited <sup>a</sup>
1	0.28	1	0.32
2	0.27	2	0.37
3	0.29	3	0.33
4	0.27	4	0.31
5	0.26	5	0.34
6	0.25	6	0.32
Average	0.27	Average	0.33
Rel. S. D.	5.2%	Rel. S. D.	±6.5%

Cd		Ni	
Run	Fraction of material deposited <sup>a</sup>	Run	Fraction of material deposited <sup>a</sup>
1	0.25	1	0.17
2	0.26	2	0.15
3	0.26	3	0.14
4	0.23	4	0.11
5	0.23	5	0.12
6	0.31	6	0.15
Average	0.24	Average	0.14
Rel. S. D.	±8.3%	Rel. S. D.	±16%

<sup>a</sup> Two-hour deposition time at potentials cited in Table 2.

used for sample introduction and analysis. All deposition potentials were sufficiently cathodic relative to  $E_{1/2}$  of the analyte species to insure maximal deposition efficiencies at all concentration ranges employed. Following deposition the wires were air dried and loaded in the exploding wire chamber for analysis.

Relative spectral intensities were obtained using a Joyce, Loebel Mark III B microdensitometer and the appropriate calibration curve for the film and wavelengths employed.

The relative concentration ranges listed in Table 2 refer to that of the metal in the 300 ml plating bath volume; while the absolute amounts seen per wire represent the actual mass of sample exploded per wire.

#### RESULTS AND DISCUSSION

The analytical curves for Cd, Ni, Hg and Pb are shown in Figs. 10–13 respectively. Each point on the Cd, Ni and Hg curves represents an average of the intensity ratios of the three wires obtained from a single plating bath. In the case of Pb, an intensity ratio is not used, and the points merely represent an average of the three Pb line intensities from any particular plating concentration. When the intensity ratios are plotted, a convenient silver line resulting from the wire emission is used. The Ag can be considered an internal standard, whose line intensities are used for normalization. However, unlike conventional internal standards, the Ag is neither introduced into the sample for the sole purpose of standardization, nor

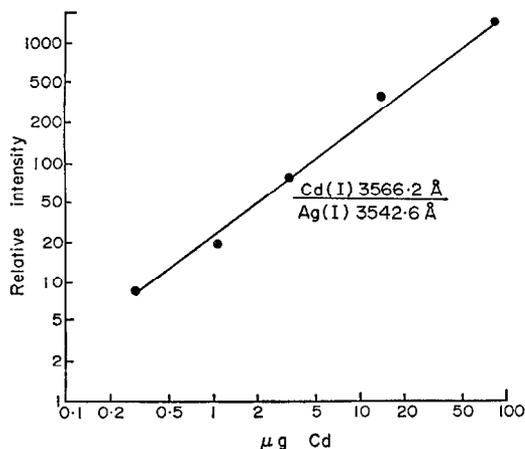


Fig. 10. Analytical working curve for Cd. Each  $\mu\text{g}$  detected on the wire corresponds to a 0.13 ppm solution in the plating bath.

is the element or its emission line chosen on the basis of thermodynamic compatibility with the analyte. Ratioing is useful here in correcting for minor motion and instability of the plasma. It should be noted that Cd, Ni and Pb all display a linear working range over approximately two orders of magnitude, despite the fact that Pb shows deviations from a straight-line relationship at high concentrations.

Mercury loss by evaporation of the deposit prior to analysis was tested as a possible cause for the curvature in the Hg working curve. A series of solutions each containing 146 ppm Hg was electrodeposited onto six sets of Ag wires. One set was allowed to hang exposed to the air for 4 days before it was exploded. The wires left exposed for extended periods of time show concentrations well within the standard deviation obtained from the other 4 sets of wires which were exploded

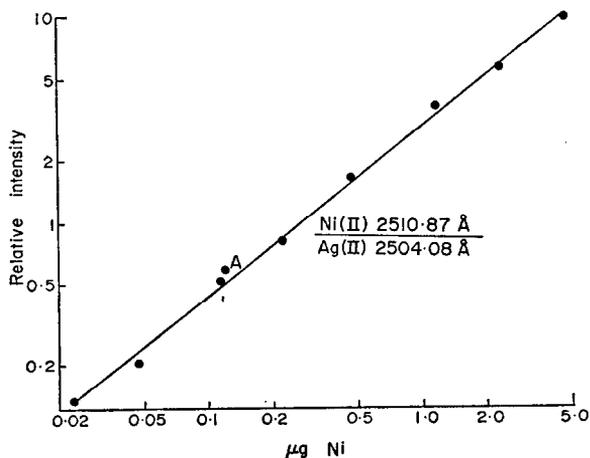


Fig. 11. Analytical working curve for Ni. Each  $\mu\text{g}$  detected on the wire corresponds to a 0.21 ppm solution in the plating bath.

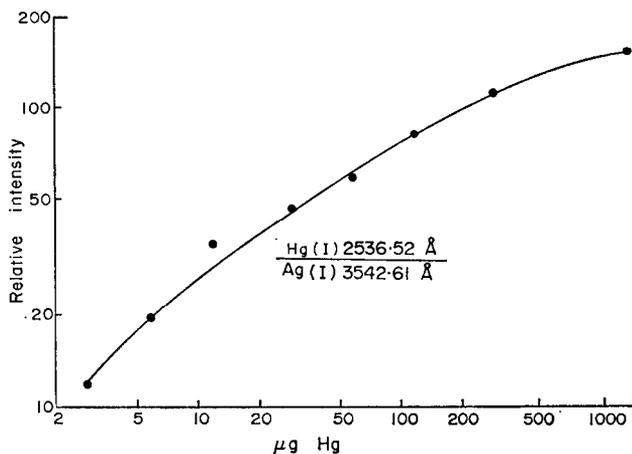


Fig. 12. Analytical working curve for Hg. Each  $\mu\text{g}$  detected on the wire corresponds to a 0.11 ppm solution in the plating bath.

immediately after deposition (*viz.* 43 ppm). Similarly, densitometer traces of both the Pb(I) 2833.1 Å and Hg(I) 2536.6 Å lines show no signs of self-absorption. However, the line widths are sufficiently narrow relative to the band pass of the instrument to warrant a complete line profile study with a high resolution instrument before any definitive statement can be made.

It should be noted that the maximum amount of Hg exploded, i.e., 1.31 mg, represents a mass of material which is 75% of the total mass of Ag wire exploded. The added energy required for vaporization and excitation could contribute to the deviation from linearity in the working curve.

### Sensitivity

Absolute detection limits at a S/N ratio greater than 2 for Cd, Ni and Pb are 10 ng, 10 ng and 15 ng, respectively. These values represent relative detection

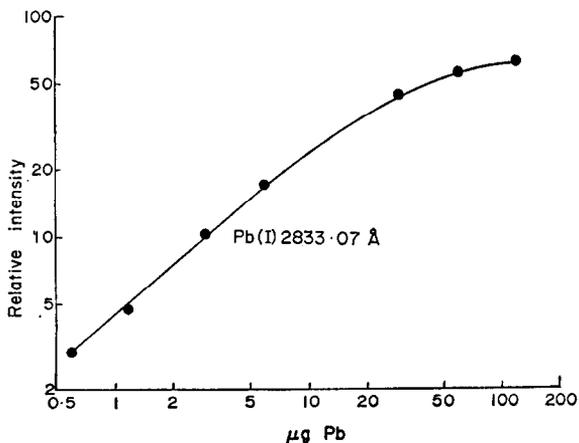


Fig. 13. Analytical working curve for Pb. Each  $\mu\text{g}$  detected on the wire corresponds to a 0.09 ppm solution in the plating bath.

limits of the solution in the plating bath of 0.001, 0.002 and 0.001 ppm for Cd, Ni and Pb, respectively. These relative limits of detection are based on the particular cell geometry, solution volume, and plating times cited here.

The presence of significant amounts of Hg impurity in the Ag wire prohibited experimental determination of a detection limit based on a S/N ratio of 2 above background noise. However, by extrapolating the working curve to lower concentrations a conservative estimate of 30 ng absolute or 0.003 ppm for a relative detection limit is predicted and should be attainable from wires with low Hg impurity.

### *Reproducibility*

The precision of the plating procedure and the overall reproducibility of the system were considered. Table 3 shows the fraction of material plated in a 2 hr period for Hg, Pb, Cd and Ni initially present at the 100 ppm, 10 ppm, 10 ppm and 10 ppm levels respectively. Atomic absorption was used to analyze the plating baths before and after deposition in the manner previously described. Concentrations of the plating bath were chosen to coincide with the optimum working range for the flame absorption work as specified in the manufacturer's literature. Reproducibility appears to decrease at higher plating potentials. This possibly is due to the simultaneous evolution of hydrogen at sufficiently cathodic potentials.

Table 4 gives the overall reproducibility of the method using the intensity of the analytical line or line ratio and converting this to apparent sample concentration. The per cent relative standard deviation from the amount added and that observed are  $\pm 26.8\%$  for Hg,  $\pm 12.4\%$  for Pb,  $\pm 17.3\%$  for Cd and  $\pm 16.8\%$  for Ni. Mercury coated wires display a marked decrease in explosion reproducibility when compared to the plating efficiency reproducibility of  $\pm 6.02\%$ . This is easily seen spectrally where a noticeable decrease in intensity of both Hg and Ag lines are observed on occasional shots. Preliminary observations suggest a possible cause of these explosion anomalies might exist in the low boiling nature of Hg which may alter the restrike to the point of severe plasma motion relative to the solid angle subtended by the spectrograph. Further studies will be required to elucidate this problem.

### *Matrix studies*

The analytical implications of a second element plated simultaneously onto the wire in at least 100 fold excess of the analyte also was considered. A series of wires each containing 20  $\mu\text{g}$  of Cd and 0.12  $\mu\text{g}$  of Ni was exploded to consider the effects of this "matrix" on the Ni analytical results. These two metals represent extremes in both ionization potentials and boiling points (see Table 2), and yet the Ni(II)/Ag(II) intensity ratio remained within experimental error of the value obtained in the absence of Cd (see point A in Fig. 11).

Controlled-potential electrolysis allows selective concentration prior to the analysis step thus providing the capability of leaving in solution those elements which may cause spectral interferences. An example where such a separation would be useful is in the analysis of trace metals in acid mine water which often contains large amounts of dissolved iron, a troublesome spectral interferent for many elements if adequate resolution in the monochromator or spectrograph is

Table 4. Overall method reproducibility

Amount added (Hg ppm)	Amount determined (Hg ppm)
162	167
162	103
162	148
162	199
162	114
	Rel. S. D. $\pm 26.5\%$
Amount added (Pb ppm)	Amount determined (Pb ppm)
0.465	0.443
0.465	0.403
0.465	0.537
0.465	0.485
	Rel. S. D. $\pm 12.4\%$
Amount added (Cd ppm)	Amount determined (Cd ppm)
0.812	0.697
0.812	0.854
0.812	0.969
	Rel. S. D. $\pm 17.3\%$
Amount added (Ni ppm)	Amount determined (Ni ppm)
0.0945	0.0744
0.0945	0.112
0.0945	0.0911
0.0945	0.0992
	Rel. S. D. $\pm 16.6\%$

not available. A known amount of Pb was added to solutions containing various amounts of  $\text{FeCl}_3$ , and a 2-hr deposition carried out at  $-0.50$  V *vs.* S.C.E. The potential for deposition was chosen from cyclic voltamograms run using the actual plating cell and Ag-wire electrode to provide the most accurate determination of the plating potential for Pb on a Ag electrode.

Lead was present consistently at the 0.25 ppm level in the sample solution, and the Fe concentration varied from 0.05 ppm to 50 ppm, i.e., up to 200 times more concentrated than the Pb. The relative amounts of Pb determined are listed in Table 5. No Fe emission lines were observed in any of the wires exploded.

The matrix studies discussed above represent successful analysis of an element in the presence of a large excess of both a reducible species Cd and a non-reducible species Fe. The successful determination of Ni, which was simultaneously deposited with a large amount of Cd, suggests that the exploding wire excitation source exhibits minimal dependency on the plated substances. These studies of codeposition and separation suggest minimal problems in the controlled potential deposition. However, specific electrode processes are extremely complex and often sensitive to adsorption and other ill-defined processes at or near the electrode surface, thus requiring further studies before the extent of matrix dependencies in the preconcentration step are fully determined.

Table 5. Separation and analysis of Pb in the presence of Fe

[Fe] [Pb]	-Pb- Amount added (ppm)	-Pb- Amount determined (ppm)
0.0	0.250	0.255
0.0	0.250	0.277
0.2	0.250	0.309
1.0	0.250	0.227
5.0	0.250	0.282
50.0	0.250	0.220
200.0	0.250	0.217
		Rel. S. D. $\pm 14.4\%$ .

## CONCLUSION

The exploding wire technique offers some attractive features which are summarized below:

1. Electrodeposition provides an effective means of preconcentration. The use of controlled-potentials and suitable masking agents affords the opportunity of selectively plating only those elements of interest while leaving behind those elements which may be the source of spectral or chemical interferences.
2. Electrodeposition minimizes the possibility of matrix effects caused by the compound form of the analyte since all samples are eventually reduced to the pure metal. Thus, such problems as the presence or formation of refractory oxides or fractional distillation of the sample are virtually non-existent.
3. In general, electrodeposition represents a useful method of extracting trace metals from aqueous solutions at the sampling site to minimize adsorption of the metals on the walls of the collection vessel. Similarly, the need for immediate analysis after collection would no longer be necessary if the sample exists as a metal coating on a wire.
4. Presented here as an emission method, the exploding wire technique offers multielement capabilities from a single explosion.
5. While the "spectral blank" from the source is rich in Ag emission lines, no band systems have been detected, thereby putting only minimal restrictions on the spectral regions available for analytical work.
6. The method is a total consumption sampling technique. This provides consistency in the sampling and excitation steps.
7. The use of the wire substrate as a built-in internal standard provides for maximal reproducibility and convenience.

Work is in progress to optimize the plating procedure for maximal efficiency and reproducibility. When certain plated elements are present on the wire in excessive amounts, *e.g.* more than 100  $\mu\text{g}$  of Ni, flaking of the deposit will occur.

Further studies include analytical consideration of a variety of other elements and an in-depth look at the various stages of the analysis including both the electrodeposition procedure and the actual mechanisms involved in the explosion. The method also will be employed in the analysis of real samples with initial efforts

being directed toward multielement analysis of trace metals found in biological samples.

*Acknowledgments*—The authors wish to express their appreciation to the National Science Foundation, Grant GP-37026, for partial support of this project. One of us (J. A. H.) wishes to acknowledge the financial aid of a National Science Foundation traineeship. In addition, we wish to express our appreciation to Dr. M. D. MORRIS for many helpful discussions and suggestions regarding electroplating procedures and the construction of the electroplating apparatus and to Mr. JOHN HUNTER who prototyped many of the electroplating procedures.