

THE SPECTROGRAPHIC SENSITIVITY OF THE LEAD SPECTRAL LINE 2833.1 A^O

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THE SPECTROGRAPHIC SENSITIVITY OF

THE LEAD SPECTRAL LINE 2833.1 A°

By

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INTRODUCTION

It was found possible by examination of very dilute solutions to detect spectrographically an amount of 209 millimicrograms of lead. The factors influencing the sensitivity of lead will be discussed in this paper. The optimum working conditions were determined by observing the variables such as: (1) diameter of electrodes, (2) means of drying, (3) effect of acid on electrodes, (4) exposure time, (5) excitation voltage, and (6) development time. The work was done by drying the solutions on pure copper electrodes and passing a high voltage spark between the electrodes. Certain copper lines from the electrodes were used as an internal standard.

On all the spectroscopic plates referred to in this discussion the inductance was 0.32 millihenries and the capacitance 0.0074 microfarads. These remained constant throughout the investigation.

Density has been defined as the Log I°/I where I° is the incident light intensity in the photometering beam, and I is the light transmitted at the plate.

The method employed concerns utilizing a definite amount of the element placed on the electrodes.

Throughout this investigation the lead line referred to will be 2833.1 A° and the copper line 2882.9 A° .

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APPARATUS

The condensed spark apparatus consisted of 110 volt A. C. source, variac, voltmeter, step up transformer consisting of a 110 volt primary producing 25,000 maximum secondary potential, capacitor, and inductance coil.

The direct current arc source was employed for an iron arc in emulsion calibration. The source was composed of a 220 volt direct current generator, voltmeter, ammeter, potential divider, and series of resistors.

The electrodes were composed of specially pure, hard copper rods, 0.25 inch in diameter. The ends were made flat by machining on a lathe. Other than iron, copper is customarily used as a metallic electrode. It acts quite differently from the iron and cannot be held steady, having a tendency to wander from place to place over the end of the electrodes. If small electrodes were used to prevent this wandering, they would become so hot that they would bend.⁽¹⁾

A Bausch and Lomb Littrow type quartz spectrograph was used in producing the photographic plates. Kodak Spectrum Analysis No. 1 emulsion type plates, 4×10 inches in size were used. These plates give a high gamma curve and result in good measurements over a limited concentration range. Kodak developer D-19 and Kodak fixer were used in a developing tank that was agitated mechanically. A water thermostat regulated the constant

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temperature at 18° C.

The Hilger microphotometer was used to measure the blackening of the different lines on the photographic plates. The deflection value of the line becomes the percent of light transmitted by the line if the clear plate reading is set at 100. A measurement such as this provides a correction for background, if present, as well as an indication for line density. Reference to the calibration curve (d/log I) of the negative will give the logarithm of intensity equivalent to this deflection. The difference between the logarithm of intensity for the standard and the unknown will bear a linear relation to the logarithm of percent of unknown element present.⁽²⁾

In passing through any spectrograph, as through any optical instrument, light is lost through absorption in the lenses and prisms and thru reflection at each surface in the optics.⁽⁶⁾

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EXPERIMENTAL

The solutions were prepared by adding 0.1599 grams of lead nitrate and diluting to 100 milliliters with 0.5% HCl (by volume). This gave a solution containing 0.1 gram of lead per 100 milliliters of solution and was considered as the stock solution. From the stock solution varying concentrations for the dilution series were made. The solutions were placed onto the electrodes by means of a measuring pipette graduated in hundredths of one milliliter. Two hundredths of a milliliter was used for each set of electrodes.

During the initial part of the investigation the cathode (copper electrode) was machined on the lathe to produce a five degree convex surface while the anodes had a five degree concave surface. This procedure was discarded in favor of the flat end electrodes for no appreciable difference in sensitivity was observed; the latter method also conserved time. The machined surface of the electrodes should be very smooth to prevent local concentration of the discharge.⁽⁴⁾ The electrodes are resurfaced after sparking to remove the oxides present.

It was found advantageous to discard the use of the more persistent lead line at 4057.1 A° in favor of using the line at 2833.1 A° . This was done because in the first case duplication of the logarithmic ratio of the lead line to the background near the line was not constant for a given concentration. The variation in some cases was greater than the readings themselves.

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The line at 4957.8 A° has an arc and spark characteristic of 2000R and 300R respectively; the 2833.1 A° line has 500R and 80R arc and spark characteristics.⁽²⁾

In an ideal procedure for quantitative spectroscopy there would exist a situation in which all elements in the matrix enter the discharge, diffuse through it, and are excited to radiation at a uniform relative rate, regardless of boiling points, atomic weights, vapor pressures, or excitation functions; or of variations in the discharge conditions; or of the time. Fortunately it is not essential to have such an ideal or absolute source.⁽⁵⁾

Carbon electrodes were arced with lead solutions but the cyanogen bands interfered with the lead lines in question; thus the copper electrodes were sparked.

The sample solutions, 0.01 mililiter, were placed on the ends of each electrode; position V on the spectrograph was utilized having a range of 2549 A° - 3641 A° . The exposures were made for sixty seconds at a primary voltage of 50 volts. The slit width was taken as 42 microns (drum setting of 7). The weight used was 3 x 10⁻⁷ grams of lead on the electrodes in all cases where the weight was considered to be constant. The diameter of the electrodes was taken as 0.25"; the samples were dried in air for one hour, acid added and dried for one additional hour.

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Table I shows that the sum of the deviations from the average values of the galvanometer deflections of the copper lines from copper electrodes less than 0.25" diametrically and two to three inches in length, was greater than the sum of the deviations for those electrodes with 0.25" diameter.

TABLE I (Plate #27)

		· · · ·							
Diameter	eter Galvanometer		deflect	deflections		deviations from mean			
	Pb	Cul	^{Cu} 2	Cuz	Pb	Cul	^{Cu} 2	Cu ₃	
< 0 .2 5"	20.8	22.5	18.9	15.7					
< 0 .2 5"	19.9	19.3	14.3	13.2					
< 0 .2 5"	20.3	21.1	17.0	14.8	2.08	7.00	8.64	3.88	
<0 .2 5"	21.4	18.2	13.2	13.7					
< 0 .2 5"	20.5	21.4	17.4	14.7					
0 .2 5"	21.0	21.5	17.5	13.5					
0 .2 5"	21.6	20.5	16.6	12.8					
0.25"	19.9	19.8	15.7	12.0	2.98	2.12	1.92	3.64	
0 .2 5"	21.4	20.8	16.5	12.5					
0.25"	22.0	20.5	16.6	14.4					
						and the state of t			

DEVIATIONS OF GALVANOMETER DEFLECTIONS

It was found that the diameter of the copper electrodes at 0.25", as compared to those of less than 0.25", had no marked effect on the density of the lead line; the density of the copper line, which was used as an internal standard, was more constant and lower at a diameter of 0.25". The electrodes that were less than 0.25" were not of uniform diameter at the sparking ends due to machining the surface on the sides of the electrodes at vary-ing depths. The electrodes had no preliminary cleaning before sparking.

Table II shows that a greater density for the lead and copper lines is obtained by reading the emulsion side of the plate on the densitometer as compared to the glass side in that the focal point is on the emulsion side causing the blackening to be more intense over a smaller area. The glass side covers a larger area for a particular line and results in a lower density value. This table also shows the consistency of the galvanometer deflections for the uniform diameters of 0.25".

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TABLE II (Plate #26)

Diameter	Er	Emulsion side				Glass side				
of Cu	Pb	Cu	D pb	Dcu	Pb	Cu	Dpb	Dcu		
< 0.25"	21.4	11.5	.1881	•4578	23.4	16.6	.1079	.2 570		
< 0.25"	23.8	20.9	.1419	.1984	25.0	22.9	.0792	•1173		
<0.25"	20.2	13.9	.2131	• 3 755	2 2.6	18.2	.1230	.21 70		
0 . 25"	24.2	19.6	.1347	.2262	25.1	21.8	•0774	•1386		
0 .2 5"	20.7	17.7	.2025	.2705	22.9	20.8	.1173	.1590		
0.25"	21.3	18.7	.1901	.24 67	23.2	21.3	.1116	. 1487		

GALVANOMETER DEFLECTIONS

A plate was made whereby half the electrodes, each pair containing 3×10^{-7} gram of lead in solution, were dried in the oven and the remaining half were dried in the air. The lead lines were absent and the copper lines were much lighter in those samples that were dried in the oven at 100° C. for twenty minutes as compared to the samples that were dried in the air at room temperature for one hour. The lead lines appeared and the copper lines were noticeably heavier in the latter case. The excitation conditions were identical. It appears that in the first case the lead nitrate combines with the moisture in the air forming a lead hydroxide and nitric acid; in the latter case the lead nitrate breaks down to lead dioxide and at 100° C. the solid is volatilized. When the

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solutions were left drying overnight or for a period of twentyfour hours, no lead lines or very faint lines appeared with no consistency.

With the excitation conditions again remaining constant, a plate was made whereby half the samples had an additional 0.1 milliliter of 1% HCl (by volume) added to the end of each electrode. The additional HCl had no marked effect on the density of the lines; the lead samples were obtained in hydrochloric acid solutions which tend to increase the sensitivity of the lead.

Sensitivity does not depend critically on the electrical characteristics of the spark source. Increase in the power leads to an increase in the initial intensity but increases the rate at which the sample is consumed and also increases the background intensity.⁽⁴⁾ With the concentration and all other variables remaining constant, a plate was made to show that the difference in excitation voltage had little effect on the sensitivity of the lead line. Excitation voltages from twenty to sixty-five were used, and it was found that at a primary voltage of fifty a minimum galvanometer deflection resulted for the lead line in question; thus a maximum density resulted. Table III data is plotted to represent Fig. 1, which shows the relationship between primary voltage and the density ratio of copper to lead. A maximum density ratio is obtained at 50 volts.

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Primary	Galvanometer	Deflection	Density	$(\log I^{\circ}/I)$	Cu
Voltage	Fb	Cu	Pb	Cu	Pb
20	27.3	24.5	.0409	•08 79	•0470
25	27.3	24.8	•0409	•0826	.0417
30	25.2	22.2	•0757	.1307	.0550
3 5	27.2	26.3	•0425	•0571 ·	.0146*
40	23.7	18.9	.1024	•2006	•098 2
45	24.5	19.5	.0879	.1871	•0992*
50	21.1	14.2	.1528	•3248	.1720
55	20.6	15.5	.1632	• 2 868	.12 36
60	22.0	18.4	•1347	.2123	•0776
65	22.5	19.1	.1249	.1961	.0712

TABLE III (Plate #31)

EFFECT OF PRIMARY VOLTAGE ON DENSITY RATIO

* Not included because of incorrect timing.

The rate at which a given element will come off varies with the individual elements. If another internal standard had been used besides copper, the maximum density ratio would have occurred at another point on the voltage scale.

With a conventional controlled spark source and a given capacitance across the secondary of the transformer there is a broad optimum value for the inductance in the oscillating circuit.⁽⁴⁾



Primary voltage

Fig. 1.- Relation between primary voltage and density ratio of Cu 2882.9 Å to Pb 2833.1 Å.

The optimum exposure time was obtained by reading the background density and line density over a varying period of time produced by a given spectra. It was found that the density of the lead line varied directly with the time in seconds up to seventy-five and upon further exposure the density of the line in question remained the same. Another plate was made whereby the lead and copper line pair was observed. A maximum of 60 seconds was obtained when the density ratio of lead to copper was plotted against the time. From Plate #43 the data for Table IV was obtained and plotted on Fig. 2. This shows the relationship between the exposure time and the density ratio of lead to copper.

TABLE IV (Plate #43)

Time	Galvanometer	Deflection	Densi	ty	Pb
(Seconds)	Pb	Cu	Pb	Cu	Cu
15	24.2	29.2	•0933	.0117	.0816
30	19.0	28.2	•1983	.0269	.1714
45	13.3	24.8	•353 2	.0826	.27 06
60	13.3	27.4	•3532	•039 3	•3139
75	13.7	26.8	•3404	•0490	.2914
90	16.0	26.8	•2730	•0490	.2240

DATA FOR DENSITY RATIOS



Exposure time

Fig. 2.- Relation between exposure time and density ratio of Pb 2833.1 Å to Cu 2882.9 Å.

It was observed that the green spark changed to a blue color at the end of 60 seconds indicating that the sample was all consumed at that time, for the blue color is due to the copper itself being sparked.

Fast emulsions are used in order to minimize the exposure times. Very fast emulsions have poor storage qualities and poor reproducibility from batch to batch, making them undesirable for quantitative work based on comparision with standard plates containing known concentrations. It is submitted that the copper spark method in general offers higher absolute sensitivity with greater reproducibility and more complete coverage using one set of conditions.⁽⁴⁾ It should be noted that on a very humid day inconsistent results were obtained.

The background readings near the measured lead and copper lines were discarded, for the blackening was not noticeable to affect the densities of the lead and copper lines.

Crane $(^3)$ investigated the developing process in order to increase the sensitivity; he found that with respect to the development time that there was no appreciable change in density of the line after two minutes with D-ll developer. The plates in this investigation were developed for three minutes in D-l9 developer at 18° C., placed in acid stop for thirty seconds, and fixed in the acid fixing bath for ten minutes, rinsed in running water for ten minutes and finally dried for five minutes on the plate drier.

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The visual methods of determining sensitivities give results of relative accuracy; this accuracy may be increased by densitometry with an internal standard, with some loss in sensitivity, the deviation depending upon the specific buffer used. On each plate an intensity calibration was made by using a motor driven step sector, the steps being in a ratio of 1:1.5. Table V from Plate #41, contains data for Fig. 3, which is the calibration curve which represents the density plotted against the logarithm of the relative exposure. The reflecting prism was always removed after sparking; the iron arc was exposed for sixty seconds utilizing a step sector necessary for emulsion calibration. The shutter was opened after the iron arc was struck and closed before the arc was broken.

TABLE V (Plate #41)

Step	p Galvanometer Deflection			D	Density		
Sector	n log 1.5	F e l	Fe2	Fez	Fe 1	Fe2	Fe-3
1	•176	25.6	27.6		•0689	•0362	
2	•352	23.3	25.5		.1097	•0706	
3	•528	20.1	22.5	27.5	•1739	.1249	•0305
4	•704	17.6	19.45	24.9	.2316	.1882	•0736
5	.880	15.3	17.3	22.2	.2924	•2391	.1234
6	1.056	14.1	15.3	19.7	•3279	•2924	•1753
7	1.232	12.4	13.5	17.6	.3837	•3468	•2243

CALIBRATION CURVE DATA (IRON ARC)

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\begin{array}{r} Fe_1 = 2813.3 \ A^{\circ} \\ Fe_2 = 2851.8 \ A^{\circ} \\ Fe_3 = 2869.3 \ A^{\circ} \end{array}
```

The highest line to background ratio occurs at the beginning of the exposure, so that the more the exposure is prolonged for a given set of conditions the poorer will be the sensitivity. There is no advantage in long exposures from the standpoint of precision, since little sample light is being contributed at the end, in contrast to the usual situation in the analysis of metal electrodes in which conditions are adjusted to give as nearly constant intensity as possible.⁽⁴⁾ There has been much controversy as to whether the arc or spark source has a greater sensitivity. McBurney⁽⁷⁾

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Fig. 3.- Plate calibration curve.

states that the high potential spark is best adapted to the quantitative analysis of metals and alloys, such as Al, Zn, and steel, where the sample is of the proper size and shape to be machined or ground to a smooth, even surface on one side; it forms one electrode while carbon is the other. Where greater sensitivity is desired, the arc is better in a given set of conditions.

For the determination of lead a working curve is shown in Fig. 4, obtained from Table VI; the data was taken from Plate #41.

TABLE	VI	(Plate	#41)
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Wt. of	Galvanomete	r deflection	Densit	У	Log intensity		
Lead _8	Pb 2833.1A°	Cu 2882.9A	(Log I	7I)			,
<u>g x 10⁻⁰</u>			Pb	Cu	Pb	Cu	Pb/Cu
			0084	1004	•		• •
20.9	29.0	23.7	.0074	.1024	0	•46	46
41.8	25.3	27.0	.0667	0457	33	. 22	. 11
	20.0		•••••	•0107	•00	•	• + +
6 2 • 7	24.9	26.8	•0736	.0510	•37	•25	.12
83.6	21.5	26.1	.1374	•0605	•58	.31	.27
104 E	1 0 E	n c n	1700	0500	70	70	40
104.0	19.0	40.4	•1/90	.0360	•10	•30	•40
125.4	17.6	26.6	2243	-0522	. 84	.26	- 58
			• • • • • • •		••••	•	
146.3	20.4	26.8	•160 2	•0490	•64	•2 5	•39 *
167.2	16.9	27.2	•2419	.0425	.89	.21	•68

WORKING CURVE DATA FOR LEAD BY SPARK METHOD

* Conditions irregular



Fig. 4.- Working curve for lead by spark method.

Various samples of water were taken to examine for lead content; a raw composition sample from the Lansing Conditioning Plant, a tap sample from the laboratory, a tap sample from an East Lansing home, and a sample from the Red Cedar River were spectrographically examined and the Pb 2833.1 A^o did not appear; the concentration must have been less than 209g x 10^{-9} gm Pb/.02 ml., if there were lead in the water samples.

SUMMARY

- 1. The spectrographic sensitivity of lead by an alternating spark excitation has been found.
- 2. Electrodes of uniform diameter tend to produce a more constant copper line when copper used as an internal standard from the electrode.
- 3. The blackening of the lead and copper lines produced on the plate varied with the humidity; on a very damp day the lines were fainter.
- 4. A working curve for low concentrations of lead has been derived.

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