A SPECTROCHEMICAL METHOD FOR THE DETERMINATION OF SELENIUM

By Claude L. Waring, Helen Worthing, and Katherine V. Hazel

Trace Elements Investigations Report 687

UNITED STATES DEPARTMENT OF THE INTERIOR
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ABSTRACT

Selenium can be determined in pyrite, chalcocite, and marcasite by a spectrochemical method that is simple, and rapid, and that requires no complicated arrangement of spectrographic equipment, or chemical pretreatment of samples. Advantage is taken of the new short-wavelength-radiation plates (Eastman) and the addition of copper oxide to enhance the selenium lines 2039.85 A and 2062.78 A. The possibility exists of determining many other elements on the same exposure of the sample.

The method has application in the range of 0.0015 to 2 percent selenium. Tests indicated an average difference from the chemical results of 0.07 percent in the few percent range, 0.03 percent in the 0.1-1.0 percent range, 0.005 percent in the 0.01-0.1 percent range, and 0.00075 percent in the 0.001-0.01 percent range. The relative accuracy over the entire range is about 7 percent of the concentration.

INTRODUCTION

Recent investigations (Coleman, 1956) have shown that selenium commonly substitutes for the sulfur in sulfides associated with the sandstone-type uranium ore deposits. To aid in the study of these selenium substitutions, a rapid spectrochemical method has been developed and is reported here. The spectrograph is an excellent tool for the selenium analyses because of the possibility of determining quantitatively or semiquantitatively on the same exposure, any of 68 elements that may be present in the sample.

Regular spectrographic procedures with the use of ordinary plates, however, lack the sensitivity needed to determine selenium in low percentages, the lower limit for detection being approximately 5 percent. The low sensitivity of this element results partly from absorption of the light energy by any quartz in the optical system, and partly by absorption of the low-wavelength light by oxygen in the air and the gelatin in the photographic emulsion. Another difficulty to be overcome is the effect of the high excitation potential of selenium, which is usually above the ionization potential of the elements forming the matrix of the sample (Harrison and others, 1948).

Feldman (1945) reported the spectrographic detection of selenium at 0.01 percent in certain samples by enhancing the line 2413 A by the addition of 10 percent of tellurium. In this procedure the selenium is concentrated by sublimation in a hard glass tube. The sublimate is collected in a molten pellet of tellurium and the pellet is analyzed spectrographically. This procedure is difficult and unsuitable for production work.

Rockenbauer and Schroll (1955) also report a spectrographic procedure, preceded by chemical treatment, that has a sensitivity of 0.001 percent. The procedure consists of dissolving the samples in fuming nitric acid, drying the salts, and sparking them at 22 volts. The spectrograms were recorded on Ilford Q-2 and Ilford 1 D. plates. No mention was made of using any spectrographic buffer to cause even burning and improve the reproducibility. By contrast, the method reported here eliminates the solution of the samples, uses a different type of excitation, and uses the addition of copper oxide to produce even burning, as well as to enhance the intensities of the selenium lines, and has the advantage of simplicity and speed.

Borovik (1949) reported a method for the detection of the halogens and selenium which was used mostly for the analysis of solutions. The solutions were dried in the lower electrode and arced. Most satisfactory lines for selenium were 5176.0, 5227.5, 2630.9, and 2778.0 A.

The results given here show that, with the method described, from 2 to 0.0015 percent selenium can be determined quantitatively by using the newly developed short-wavelength-radiation plates (Eastman) and adding copper oxide to enhance the selenium line pair at 2039.85 A and 2062.78 A. This range of sensitivity includes most of the samples received in this laboratory for selenium analysis.

The samples and synthetic or chemically analyzed standards were mixed separately with 40 milligrams of copper oxide and arced for 90 seconds. The quantity of sample and copper oxide and the arcing time were established experimentally. The plates were processed, the lines were microphotometered, percentage curves were prepared, and the results calculated.

STANDARDS

A base of marcasite was used for the preparation of standards. Marcasite is iron disulfide consisting of 53.4 percent sulfur and 46.6 percent iron plus traces of other elements. Chemical analysis of this material showed it to contain < 0.0003 percent of selenium. Spectrographically pure selenium metal was ground in a boron carbide mortar to pass a 200-mesh screen. The selenium powder was added to the marcasite to make standards of the desired selenium percentages. The powders were thoroughly mixed by passing them through a 100-mesh screen approximately 20 times. Some standards needed extra mixing as shown when the intensity ratios did not line up properly on the curve. This method of mixing powders was shown to be satisfactory in previous work (Waring and Worthing, 1953). Helz and Scribner (1947) also described a similar method for the thorough mixing of spectrographic powders.

Chemically analyzed samples of pyrite and chalcopyrite were also used as bases for standards.

EXPERIMENTAL DATA

A series of experimental arcings were first conducted to determine the time required for all selenium to be volatilized. Chemically analyzed samples of pyrite and chalcopyrite were used as matrices for this work to determine the optimum spectrographic conditions. During these tests it was noted that the same percentage of selenium in chalcopyrite as in pyrite produced quite different line intensities indicating that the presence of copper in the chalcopyrite may enhance selenium intensities. To confirm this increase in intensity tests were conducted with copper oxide and copper sulfide; little or no difference in selenium-line intensity was observed whether the oxide or the sulfide was used. It was also noted that the addition of copper oxide to chalcopyrite produced no noticeable change in line intensity. It was established experimentally that when the selenium percentages were equal the addition of 40 milligrams of copper oxide to the pyrite produced the same line intensity as the chalcopyrite without additional copper oxide. Further addition of copper oxide to the pyrite and to the chalcopyrite produced no noticeable increase in intensity (fig. 1).

Emulsion calibration curves were not prepared because of the additional problems in calibrating this new type of emulsion. Closely bracketing the samples with standards gave good quantitative results. The working curve is a plot of percent selenium versus blackening of the 2039.85 A selenium line (fig. 2).

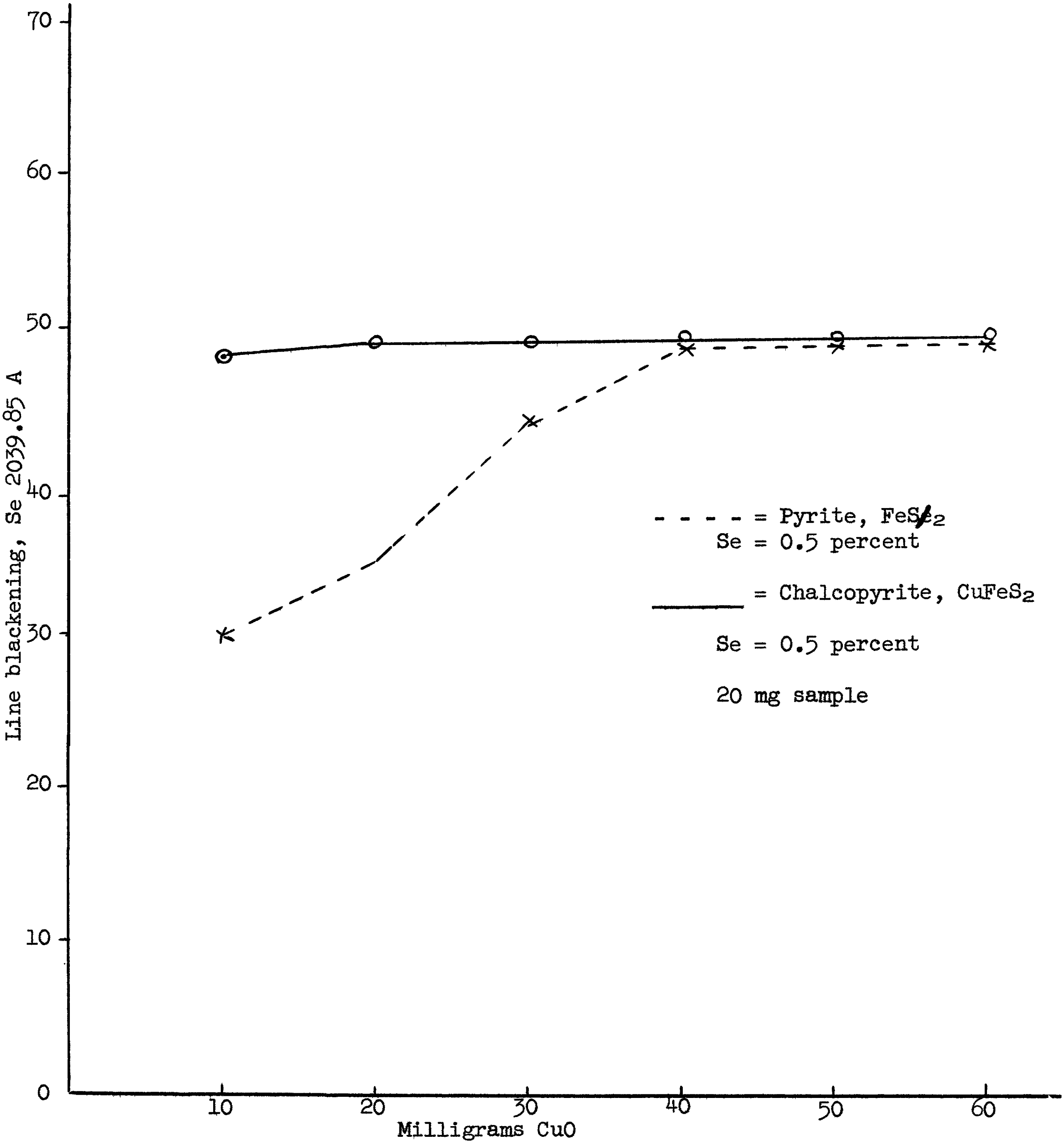

Figure 1.--Selenium blackening with addition of copper oxide.

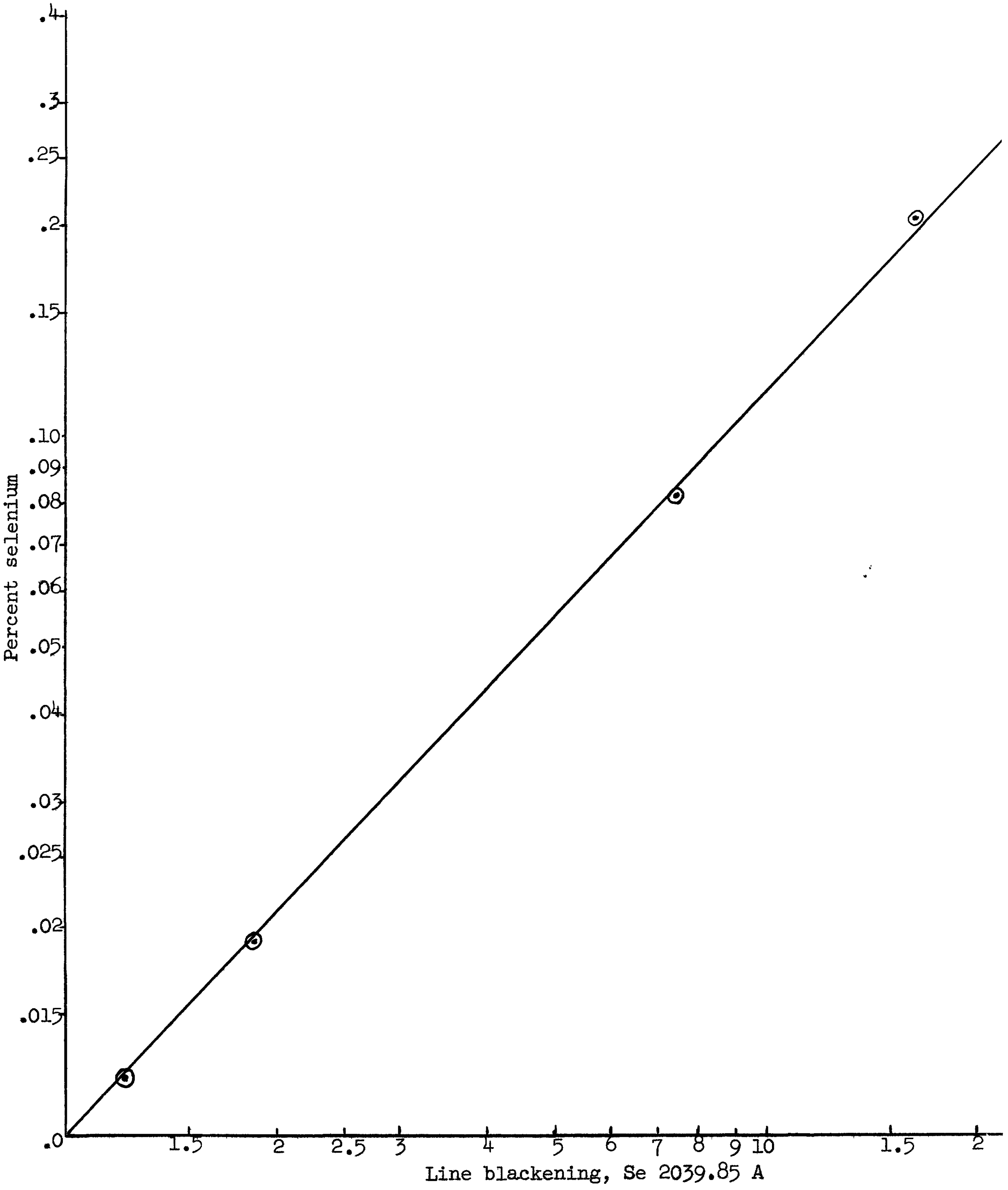

Figure 2.--Working curve for selenium.

Two spectrographs with different power sources were used with the following experimental conditions:

Spectrograph:	21-foot Wadsworth-mounted grating.	3-meter eagle-mounted grating.
Power source:	multisource, 300 volts d-c, 12 amperes.	Baird, 50 volts d-c, 12.5 amperes.
Slit:	25 microns.	25 microns.
Optics:	arc focused on collimating mirror.	arc focused on grating.
Emulsion:	S. W. R. plates.	
Development:	4 minutes at 18° C ± 0.5° C, D-19 (½ strength).	
Arc gap:	4 to 6 mm gap adjusted manually to positions on outside target.	
Transmission:	varied according to percent of selenium sought.	
Arcing time:	90 seconds.	
Spectrum:	first order.	
Electrode, lower:	spectroscopic carbon, 0.25 in., cut to outside diameter 0.22 in., depth of shoulder 0.22 in., inside diameter 0.19 in., depth of crater 0.20 in.	
Electrode, upper:	spectroscopic carbon, 0.25 in., hemispherical, 0.06-in. radius.	

ACCURACY

The accuracy of the method was checked by analyzing 15 samples of pyrite, chalcocite, and marcasite. A comparison of the chemical and spectrochemical results is given in table 1. The chemical procedure consisted of decomposing the samples with acids, distilling the selenium from hydrobromic acid - bromine solutions, reducing the selenium to the elemental form and either turbidimetrically comparing the samples with standards or filtering and weighing. The tests indicated an average difference between chemical and spectrographic results is 0.07 percent in the few percent range, 0.03 percent in the 0.1-1.0 percent range, 0.005 percent in the 0.01-0.1 percent range and 0.00075 percent in the 0.001-0.01 percent range. The relative accuracy of the method is about 7 percent of the concentration.

Table 1.--Comparison in percentage of the chemical and spectrochemical results.

Sample no.	Mineral	Location	Method		
			Spectrochemical	Chemical	Difference
97-RGC-55	Chalcocite	Cougar mine, San Miguel County, Colorado	1.65	1.70	0.05
96-RGC-55A	Chalcocite	Cougar mine, San Miguel County, Colorado	2.0	1.90	0.1
WA-2	Chalcocite	Unknown	1.65	1.72	0.07
88-RGC-55	Marcasite	J. J. mine, Montrose County, Colorado	0.18	0.21	0.03
100-RGC-55	Chalcocite	Cougar mine, San Miguel County, Colorado	0.47	0.42	0.05
WA-1	Pyrite	Unknown	0.50	0.5	0.0
C-3-55	Marcasite	J. J. mine, Montrose County, Colorado	0.50	0.55	0.05
84-RGC-55	Pyrite	Pitchfork mine, San Miguel County, Colorado	0.016	0.019	0.003
127-B-RGC-55	Pyrite	A. E. C. No. 8 mine, Emery County, Utah	0.010	0.012	0.002
91-RGC-55	Pyrite	Virgin No. 2 mine, Montrose County, Colorado	0.010	0.009	0.001
WA-3	Pyrite	Unknown	0.076	0.064	0.012
WA-4	Pyrite	Unknown	0.018	0.02	0.00
AW-53-55	Pyrite	Blackstone mine, Grand County, Utah	0.090	0.081	0.009
IRGC-55	Pyrite	Blind River, Ontario, Canada	0.0025	0.003	0.000
204-RGC-55	Pyrite	Vitro mine, Fremont County, Wyoming	0.005	0.006	0.001

DISCUSSION

The short-wavelength-radiation plates require special handling because any pressure on the emulsion will produce a black spot when developed. This problem was overcome by preventing contact of the emulsion with the black wrapping paper or with fingers. Manufacturers of the plates suggest that the short stop bath should be eliminated from the development process because the thin emulsion has a tendency not to adhere to the glass plate when this bath is used. It is recommended that development procedures be practiced before attempting to use the short-wavelength-radiation plates.

The method is limited to some extent by the amount of sample available. If the history of the sample is not known, a preliminary test using 40 milligrams of sample is required. This test will set the range above or below the 0.01-0.1 percent range. If the range is below this bracket, it is then necessary to arc 80 milligrams of the sample with suitable standards. Table 2 shows the sample weights used. In the application of the method, 40 milligrams of copper oxide is added, regardless of the sample weight. The method has not been applied to materials other than pyrite, chalcocite, and marcasite. It is expected that the method will be extended to include galenas and other types of materials. With the addition of copper oxide to enhance the spectrum in the low ultraviolet, and the short-wavelength-radiation plates to record the selenium lines 2039.85 A and 2062.78 A, this method is expected to have wide application.

The M. I. T. wavelength tables list a tellurium line at 2039.79 A with an intensity of 300. To determine if the tellurium line interferred with the selenium line 2039.85 A, pure tellurium oxide was arced under the same spectrographic conditions as these tests and the tellurium line was not visible on the plate. We are of the opinion that no tellurium line exists at 2039.79 A as listed in the M. I. T. tables.

Work is continuing to increase the detectability of selenium toward one part per million.

Table 2.--Sample weights for the different selenium percentages.

Milligrams of sample	Range percent selenium
10	1.-10.
20	0.1-1.
40	0.01-0.1
80	0.001-0.01

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