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THE MICROSPECTROCHEMICAL ANALYSIS OF MINERALS II[1]

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ABSTRACT

Modifications are made in the previously described microspectrochemical method for the analysis of minerals. By altering the type of lower electrode to allow the arc to strike the sample more directly and consume less carbon, a significant reduction in the background is observed. The period of exposure of the red portion of the spectrum is also changed. The combined effect is to lower the limits of detection for sixteen elements, four by a factor of 100. The improvements also widen the application of the method to the analysis of other types of samples.

INTRODUCTION

In the process of identifying minerals, it is often necessary to provide estimates on the chemical composition of the minerals by using a limited amount of sample. The microspectrochemical method previously described by Waring and Worthing (1961) provides these data, in conjunction with *x*-ray diffraction, to help the identifications.

Some types of minerals, such as, carnotite, leucite and muscovite, produce spectrograms with usable but objectional background intensities when the microspectrochemical method is used. Studies have continued for the purpose of finding a set of spectrographic conditions that would reduce or eliminate this background and also lower the limits of detection of as many elements as possible. Lowering the background is accomplished by altering the lower electrode to permit less carbon to be consumed during the first 15 seconds of the arcing period while the alkalies are vaporized into the arc. It is found that this reduction in carbon consumption is insufficient to vary the reproducibility to any noticeable extent. The modified method is adopted with the result that detectabilities of the following 16 elements are increased: K, Li, Mg, and Na, by a factor of 100, Al, Cr, Cs, Cu, Mn, Rb and Ti, by a factor of 10, and Ba, Ca, Ni, by a factor of 5.

The improved detection limits and decreased background have increased the scope of the method to the possibility of applying it to certain types of rock samples for elements present in minor to trace amounts. Unknown mineral samples weighing less than 0.1 mg can also be analyzed with adequate precision.

APPARATUS

The apparatus used in the tests remains unchanged with the exception of the modified lower electrodes, described as follows:

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TABLE 1. APPROXIMATE VISUAL DETECTION LIMITS, IN PER CENT, FOR THE ELEMENTS DETERMINED BY THE MICROSPECTROCHEMICAL METHOD, BASED ON 1 MG OF SAMPLE

Ag	0.0018	F	0.56	Nb	0.18	Sr	0.056
Al	0.0018	Fe	0.018	Nd	0.18	Ta	0.56
As	0.56	Ga	0.018	Ni	0.056	Tb	0.18
Au	0.018	Gd	0.18	Os	0.56	Te	10.0
B	0.056	Ge	0.056	P	0.56	Th	0.56
Ba	0.018	Hf	0.56	Pb	0.056	Ti	0.0018
Be	0.018	Hg	0.56	Pd	0.018	Tl	0.56
Bi	0.018	Ho	0.056	Pr	0.56	Tm	0.018
Ca	0.018	In	0.018	Pt	0.018	U	0.56
Cd	0.18	Ir	0.56	Rb	0.0056	V	0.018
Ce	0.18	K	0.00056	Re	0.18	W	0.56
Co	0.018	La	0.05	Rh	0.18	Y	0.018
Cr	0.0018	Li	0.00018	Ru	0.56	Yb	0.0018
Cs	0.018	Lu	0.056	Sb	0.56	Zn	0.18
Cu	0.0018	Mg	0.00056	Sc	0.018	Zr	0.18
Dy	0.18	Mn	0.0018	Si	0.056		
Er	0.18	Mo	0.018	Sm	0.56		
Eu	0.18	Na	0.00018	Sn	0.056		

Electrodes, lower, $\frac{1}{4}$ in. pure spectroscopic graphite rod $1\frac{1}{2}$ in long. Crater, outside diam. 0.225 in, depth 0.056 in, angle 120°.

STANDARDS

The chemical composition and the method of preparation of the standards remain unchanged, except that further dilutions were made. Each element grouping is used to prepare a standard plate. The electrodes are loaded with 1 mg of the standard mixture containing 10, 5.6, 1.8, 0.56, 0.18, 0.056, 0.018, 0.0056, 0.0018, 0.00056, and 0.00018 per cent of each element. These electrodes are arced to completion at 8–9 amperes and 220 volts. Iron and aluminum alloy are also arced on each plate for reference spectra.

PROCEDURE FOR SAMPLES

With the aid of a polished stainless steel funnel, 1 mg or less of sample is placed in a prepared electrode and arced at 8–9 amperes, 220 volts, for a period of 80 seconds. Appropriate reference material is arced under identical conditions. The special shutter controlling the red portion of the spectrum remains open only during the first 15 seconds of the arcing period. Many tests with the shallow electrode show that the alkalies pass into the arc stream completely during the first 15 seconds of arcing. If any of the refractory elements can be seen on the electrode at the end of 80 seconds, the same electrode is re-arced at a new position on the plate.

Visual estimates of the percentages of the elements in the sample are made by comparison with the same lines on previously prepared standard plates. A hand lens with a millimeter scale or a comparator is used to make the estimates.

The results are reported in the following precentage brackets: >10, 10 to 3, 3 to 1, 0.3 to 0.1, etc.

When fluorine is to be estimated, 0.2 mg of calcium is added to a second electrode with the unknown sample and arced. The estimate is based on the intensity of the calcium fluoride band.

SPECTRAL LINES

A wide variety of spectral lines are listed in the original paper and need not be repeated here. Two excellent lines for sodium, 8183.270 Å, and 8194.811 Å should be added to the table.

Table 1 lists the detectabilities of the elements based on 1 mg of sample. The detection limits vary according to the chemical composition of the samples and those listed are useful as a guide. These limits are based on the strongest visible lines produced by the elements in the lowest standard.

COMPARATIVE RESULTS

Four minerals previously reported were reanalyzed by the modified method to give a better basis for comparison.

Only a relative quantitative interpretation should be attached to the visual estimates provided by the method. The microspectrochemical results should be added to the *x*-ray diffraction or chemical data before any final identification is made.

REFERENCE

WARING, CLAUDE L. AND WORTHING, HELEN W. (1961), The microspectrochemical analysis of minerals. *Am. Mineral.*, **46**, 1177.

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