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MICROSPECTROCHEMICAL ANALYSIS OF MINERALS*

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ABSTRACT

A rapid microspectrochemical method is presented for the estimation of 68 elements from a single arcing of 1 mg. or less of sample.

The results are obtained through visual estimates of line intensities based on synthetic powder standards and reported in percentage brackets of 10 to 3, 3 to 1, 1 to 0.3, etc. No attempt is made to attain any high degree of detectability because a knowledge of the trace element content is not necessary for mineral identification.

A spectrographic emulsion with high speed in the red part of the spectrum and low speed in the ultraviolet part was adapted to these procedures by installing an extra slide in the plateholder. This slide permitted limited exposure of the high wavelengths while the alkalies were in the arc vapor and at the same time the ultraviolet part was exposed during the total arcing period.

INTRODUCTION

Microspectrochemical analysis is used commonly in the Geological Survey laboratory in conjunction with *x*-ray diffraction methods for the identification of unknown minerals and as an aid in selecting chemical procedures when a limited amount of sample is available.

In the past, the spectrographic procedures described by Stich (1953) were used to aid the mineral identifications. The techniques applied to the I-L (Eastman) type of spectrographic plates which responded equally well to the ultraviolet and red portions of the spectrum (2000 to 10,000 Å). It is necessary to cover the range of the spectrum in one arcing of the limited sample. This makes it possible to estimate the percentage of all significant elements present. The discontinuance of the I-L plates by the manufacturer created a problem with reference to continuing the spectrochemical analyses of small mineral samples.

The manufacturer has recommended the I-N (Eastman) type of spectrographic emulsion to replace the I-L series. Tests with the I-N plates have shown this type to be out of balance, when the conditions Stich used were applied to identifying small mineral samples, because of the great speed in the red part of the spectrum and diminished response in the ultraviolet. For example, a set of spectrographic conditions that gave enough intensity for the identification of B, Si, Be, and other elements in the ultraviolet would completely overexpose K, Na, Li, Rb, and Cs in the red part of the spectrum. In order to find a suitable method for the 1-N plates, many unsuccessful tests with filters were made. By in-

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stalling a special slide in the plateholder, permitting the principle of photographic dodging to be applied, a better balance was obtained.

The results by the techniques described are especially useful in distinguishing between similar minerals such as autunite, torbernite, saléeite, and to aid in the identification of metamict specimens. The information provided has a high degree of reliability because no compounds are added to the samples prior to arcing, and it is possible to correlate *x*-ray and spectrographic data on the same material.

APPARATUS

Spectrograph, medium quartz, dispersion varying from 4.6 Å/mm. at 2500 Å to 11.5 Å/mm. at 7000 Å. Special opaque slide installed in plateholder in addition to the regular slide.

Excitation source, full wave mercury vapor rectifier, 220 volts, 15 amperes maximum, inductance for smooth operation of arc, rheostat for controlling the current, connected in series with the arc. The rheostat has three fixed positions of 74, 38, and 19 ohms, producing 2, 4, and 9 amperes.

Neutral filters

Viewing box; magnifier or comparator.

Developing equipment, rocking development tank, plate washer and drier.

Electrodes, lower ¼ in. pure spectroscopic graphite rod 1½ in. long.

Crater, outside diameter	0.223 in.
Crater, inside diameter	0.193 in.
Crater, depth	0.180 in.
Outside shoulder below crater rim	0.44 in.

Electrode, upper, ¼ in. pure graphite rod, cut to 0.06 in. hemispherical radius.

Precision balance

Iron rod, ¼ in. pure as obtainable for reference spectra.

Aluminum alloy, used as reference, and standard if composition is known.

STANDARDS

The method of preparing standards was first suggested by Murata (in Fleischer, Murata, Fletcher, and Narten, 1952) and later by Bastron and others (1960). These standards are known as the pegmatite type, and the base consists of 60 parts of purified quartz, 40 parts of microcline, and 1 part of Fe_2O_3.

The elements to be sought are added to the matrix as pure oxides and thoroughly ground in agate or boron carbide mortars. For example, the elements Cu, Ni, Co, Ti, Mn, and Zr, which have similar burning characteristics and often occur together in nature, are added to pegmatite base to make one stock standard. For the micro work covering 69 elements, 20 stock standards were prepared and their groupings are shown in Table 1. The element groupings were diluted with pegmatite base to produce concentrations of 10, 5.6, 1.8, 0.56, 0.18, 0.056 and 0.018 per cent

TABLE 1. ELEMENT GROUPINGS USED IN THE PREPARATION OF MICROSPECTROCHEMICAL STANDARDS

Standard No.	Element groupings	Standard No.	Element groupings
1	W, Tl, Ru, Os, Ir	11	Rb, Cs, K, Li
2	Sc, Ge, B, Pb	12	Th
3	Sn, Mo, Be, Re, Cr, V	13	U
4	Hf, Mg, Sr, Ca, Ba	14	Pt, Pd, Rh, Au, Ag
5	Ga, Al	15	In, Zn, Sb, Bi, Cd
6	Tm, Tb, Lu, Ho, Eu	16	Te, P, Hg, As
7	Si	17	Na, Li, Cs, Rb
8	Sm, Pr, Nd, La, Ce	18	Zr, Cu, Mn, Ni, Ti, Co
9	Yb, Er, Gd, Dy, Y	19	Fe
10	Ta, Nb	20	F

of each element. These element percentages are the approximate midpoints of the brackets 10 to 3, 3 to 1, etc.

The elements Si, K, Al, and Fe require special standards because they are present in the matrix material. The Si standard matrix consisted of 8.8 parts Al_2O_3, 1 part Na_2CO_3, and 0.2 part Fe_2O_3. The K standard matrix components were: quartz, 8.1 parts; Al_2O_3, 0.88 part; Na_2CO_3, 1 part; and Fe_2O_3, 0.1 part. The Al matrix consisted of quartz, 25 parts; Na_2CO_3, 3 parts; $CaCO_3$, 1.7 parts, and Fe_2O_3, 0.3 part. The Fe matrix ingredients were quartz, 9.1 parts; Al_2O_3, 0.88 part; and Co_3O_4, 0.1 part. The matrix composition of the standards for these elements has been found satisfactory for the identification work on the basis of previous tests.

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, and 0.018 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.

The following source and plate processing conditions are used:

Resistance	19 ohms
Amperes	8–9
Spectrograph	medium quartz
Slit	10μ
Optics	arc focused on collimating lens
Emulsion	I-N (Eastman)
Development	4 min. at 18° C. $\pm\frac{1}{2}$° C., D-19
Gap	5–6 mm.
Transmission	40% (neutral filters)

TABLE 2. SPECTRAL LINES USED IN THE MICRO-SPECTROCHEMICAL METHOD
Wave lengths in Å

Ag
3280.7
3382.9
5465.5

Al
2568.0
2575.1
2652.5
2660.4
3059.9
3082.2
3092.7

As
2288.1
2349.8
2860.5
2780.2
2898.7
2492.9

Au
2675.9
2427.9
3122.8
2748.3
2700.9
2641.5
2352.7

B
2496.7
2497.8

Ba
4934.1
6141.7
5853.7
3071.6
2634.8
5535.5
4554.0
2335.3

Be
3131.1
3130.4
2348.6
3321.3
2350.7

Bi
3067.7
2938.3
2897.9
3024.6
2989.0
2780.5
2627.9

Ca
4226.7
3179.3
3158.9
8542.1
8662.1
8498.0
4456.6

Cd
3261.1
2980.6
2288.0
2265.0
4799.9
2981.3
2836.9
3466.2
2763.9

Ce
4222.6
3272.3
3056.8
3055.2
2651.0
4186.6
4040.7
4012.4

Co
3453.5
3412.6
3412.3
3044.0
2521.4
2663.5
2649.9
2519.8
3465.8
3449.2
3283.5
3243.8

Cr
4289.7
4274.8
4254.3
2843.3
2835.6
2860.9
2855.7
2769.9
2731.9

Cs
8521.1
4593.0
4555.5
3347.4
3247.5

Cu
3274.0
3247.5
2618.4
2492.1
2766.4
2441.6
2824.4
2293.9

Dy
3407.8
3393.6
3385.0
3280.1
3251.3
3645.4
3454.3

Er
3264.8
3230.6
2964.5
4419.6
3499.1
3372.8

Eu
2813.9
2906.7
2727.8
2665.6
2678.3
2814.0
2816.2
4435.6

F
CaF_2
Band
Heads
5291.0
6036.9
6064.4

Fe
3020.6
2599.4
2739.5
2598.4
3100.3
3099.9
3099.8
2598.4

Ga
2943.6
2944.2
2874.2
2719.6
2500.2

Gd
3100.5
3034.1
3032.8
3027.6
2840.2
2809.7
3671.2
3646.2
3358.6
3082.0

Ge
3039.1
2651.6
2651.2
3269.5
2691.3
2740.4
2589.2
2533.3

Hf
3134.7
3072.9
3012.9
2861.7
2861.0
2683.4
2531.2
2820.2
2773.4

Hg
2536.5
3131.8
3131.5
3125.7
4358.3
3650.2

Ho
3456.0
3453.1
3416.5
3398.9
4254.4

In
3256.1
3039.4
3258.6
2753.9
2710.3
4511.3

Ir
3220.8
2639.7
2543.9
2534.5
2533.1
2664.8
2849.7
2924.8

K
7698.9
7664.9
4047.2
4044.1
3447.7
3446.4

La
3337.5
3344.6
3303.1
3265.7
2808.4
2610.3
3380.9
4333.8
4429.9

Li
6707.8
6103.6
3232.6
2741.3

Lu
3077.6
2615.4
2619.3
2613.4
2685.1
2392.2
2911.4
3198.1

Mg
2852.1
2802.7
2795.5
2782.9
2779.8
2776.7
4351.9

Mn
2576.1
2605.7
2593.7
2939.3
2933.1
3044.6
2584.3
2798.3

Mo
3193.9
3170.3
2816.2
3208.8
3158.2
2784.9
2763.6
4251.9

Na
5895.9
5889.9
3302.9
3302.3

Nb
3225.5
3094.2
2931.5
2876.9
2875.4
2746.1
2745.7
3358.4

Nd
4303.6
4247.4
3328.3
3275.2
4325.8

Ni
3050.8
3002.5
2992.6
2943.9
2907.5
2798.7
3492.9
3433.6
3414.8
2320.1

TABLE 2—(*continued*)

Os
3058.7
2909.1
3301.6
2838.6

P
2553.3
2535.7
2554.9
2534.0

Pb
2833.1
2802.0
2614.2
2873.3
2823.2
2663.2
2393.8

Pd
3421.2
3242.7
3251.6
2763.1
3002.7
2922.0
3114.0
3634.7

Pr
4241.0
4225.3
5322.8
5259.7
4206.7

Pt
3064.7
2997.9
2659.5
2650.8
2646.9
2803.2
2639.4
4242.6
3042.6

Rb
7947.6
7800.2
4297.7
3436.7
3428.3
2810.6
2810.0

Re
3464.7
3460.5
2715.5
2674.3

Rh
3434.9
3396.9
3283.6
3280.6
3271.6
3263.1
4374.8

Ru
2874.9
2735.7
2678.8
2886.5
2734.3
2810.0
2810.6
3428.3
3436.7
4297.7

Sb
2598.1
2877.9
2769.9
2718.9
2670.6
3267.5
2528.5
2311.5

Sc
2560.2
2552.4
2555.8
2545.2
2822.1
3019.3
3369.0
3907.5
3911.8
4246.8

Si
2881.6
2516.1
2987.6
2435.2
2532.4
2438.8
2528.5
2524.1

Sm
3273.5
3272.8
3254.4
3254.3
3253.9
4256.4
4424.4

Sn
3034.1
2839.9
3009.1
2863.3
2850.6
2661.2
2571.6
3262.3
3175.0

Sr
4607.3
3464.5
4305.4
3380.7
3351.3
2569.5

Ta
2685.1
2635.9
2714.7
2675.9
2902.0
2891.8
4574.3
3642.1
3317.9
3311.2
3012.5

Tb
4278.5
3324.4
3219.9
3218.9
3293.1
4318.9

Te
2385.8
2383.3

Th
2837.3
2832.3
2870.4
2842.8
2703.9
2565.6
4391.1
4619.5
4019.1
3108.3
2752.2

Ti
3241.9
3239.0
3236.6
3234.5
3088.0
3078.6
3072.9
3072.1
2956.1
2941.9
2619.9
2605.2
3372.8
3224.2
3088.0

Tl
2767.9
5350.5
2918.3
3775.7
3529.4
3519.2
2767.9
2379.6

Tm
3133.9
3131.3
4242.2
3462.2
3362.6
3151.3
3362.6

U
4244.4
4241.7
2882.7
4287.9
3566.6
2837.3
2837.2

V
3185.4
3183.9
3183.4
3202.4
3198.0
3214.7
3212.4
4379.2
3276.1
3267.7
3184.0

W
2946.9
2444.4
2947.4
2589.2
4302.1
4294.6
3049.7

Y
3242.3
3216.7
3200.3
3195.6
2984.3
2422.2
3086.9
3055.2
3327.9

Yb
3289.4
2970.6
3031.1
2653.8
3107.9
2891.4
3988.0

Zn
3345.0
3302.6
3282.3
2800.9
4810.5
2770.9
2770.8
4680.1

Zr
3438.2
3391.9
2758.8
2752.2
2889.4
2888.0
3556.6
3273.0

PROCEDURE FOR SAMPLES

A 1 mg. or less sample is weighed and placed in a prepared electrode with the aid of a stainless steel funnel. The sample is subjected to a direct current arc of 8–9 amperes for a period of 80 seconds. Iron and an aluminum alloy are also arced under similar conditions to produce reference spectra. The special shutter on the plateholder is opened at 22 seconds

TABLE 3. APPROXIMATE VISUAL DETECTION LIMITS FOR THE ELEMENTS DETERMINED BY THE MICROSPECTROCHEMICAL METHOD, BASED ON 1 MG. OF SAMPLE

Element	%	Element	%	Element	%
Ag	0.018	Hf	1.8	Re	0.18
Al	0.056	Hg	0.56	Rh	0.18
As	0.56	Ho	0.056	Ru	0.56
Au	0.018	In	0.018	Sb	0.56
B	0.056	Ir	0.56	Sc	0.018
Ba	0.056	K	0.018	Si	0.056
Be	0.018	La	0.056	Sm	0.56
Bi	0.018	Li	0.018	Su	0.056
Ca	0.056	Lu	0.056	Sr	0.056
Cd	0.18	Mg	0.018	Ta	0.56
Ce	0.18	Mn	0.018	Tb	0.18
Co	0.018	Mo	0.018	Te	10
Cr	0.018	Na	0.018	Th	0.56
Cs	0.56	Nb	0.18	Ti	0.018
Cu	0.018	Nd	0.18	Tl	0.56
Dy	0.18	Ni	0.056	Tm	0.018
Er	0.18	Os	0.56	U	0.56
Eu	0.18	P	0.56	V	0.018
F	0.56*	Pb	0.056	W	0.56
Fe	0.018	Pd	0.018	Y	0.018
Ga	0.018	Pr	0.56	Yb	0.018
Gd	0.18	Pt	0.018	Zn	0.18
Ge	0.056	Rb	0.056	Zr	0.18

* A second exposure is required for the fluorine determination.

and closed at 62 seconds, exposing the alkali portion of the spectrum one half of the total arcing time. Some refractory elements, such as Nb, Ta, and Zr, require a second burn of the same sample.

When the sample is very limited, the *x*-ray spindle is weighed and a previously determined blank is subtracted. The spindle, frequently containing as little as 0.01 mg. of sample, is placed in the electrode cup and arced.

After the plates are processed, the quantities of unknown elements are estimated by visual comparison of certain lines of the elements in question with those on previously prepared standard plates. Two methods are available to the operator for viewing the lines. The hand lens with a millimeter scale and an enlargement of approximately ten times is preferred by some operators. Also, the standard plates and the unknown plates may be placed in a comparator in juxtaposition with an enlargement of approximately twenty times.

The results are reported in the following brackets: 10 to 3, 3 to 1, 0.3 to

TABLE 4.—COMPARISON OF CHEMICAL[1] AND MICROSPECTROCHEMICAL ANALYSES OF MINERALS[2]

Element	Kimzeyite		Valleriite		Corvusite-like mineral		Sherwoodite	
	Chemical[2]	Spectrochemical	Chemical[2]	Spectrochemical	Chemical[2]	Spectrochemical	Chemical[2]	Spectrochemical
Si	4.5	3	0.84	1	0.3	0.3		
Al	5.5	3	4.3	1			1.3	1
Fe	9.9	>10	21.2	>10	1.6	3	.5	.3
Mg	< .03	.01	9.8	>10			.3	.3
Ca	21.4	>10	1.2	1	1.7	3	9.3	>10
Mn	< .08	.03	< .04	.01				
Ti	3.3	3						
Zr	22.2	>10						
Nb	.7	1						
Cu			17.6	>10				
V					44.1	>10	31.8	>10

Element	Metaheinrichite		New calcium vanadyl vanadate		Abernathyite	
	Chemical[2]	Spectrochemical	Chemical[2]	Spectrochemical	Chemical[2]	Spectrochemical
Fe	1.03	1	<0.07	0.03		
Ca	.07	.03	6.0	3		
K					3.6	3
Ba	11.9	>10				
U	43.6	>10			49.2	>10
As	9.5	>10			21.8	>10
Pb	.7	.3				
V			38.8	>10		
Sr			.85	1		

[1] Chemical analyses by Robert Meyrowitz and Blanche L. Ingram; results as oxides converted to elements.

[2] These minerals have been studied by x-ray diffraction patterns by Daphne R. Ross.

0.1, etc. When less than 1 mg. of unknown is arced, the results are adjusted by the appropriate factors.

The estimation of fluorine, the 69th element on our list, requires a separate exposure. An excess of calcium (0.2 mg.) is added to the electrode containing the unknown to produce the calcium fluoride molecular band which is recorded by the photographic emulsion.

SPECTRAL LINES

The lines used for the estimations were selected from the M. I. T. Wavelength Tables (Harrison, 1939), and are listed as follows in Table 2, in order of decreasing usefulness. The percentage range for each line is not included because the wide variety of materials usually tested, and the interferences encountered, affect the sensitivities of the lines. Many different wavelengths are included to help the operator cross-check his results and also to allow for interferences.

The detectabilities of all elements are shown in Table 3. The percentages shown represent the lowest concentration detectable in the standard. Some combinations of elements affect the detectabilities; therefore approximate values are given. In unusually favorable materials, concentrations somewhat lower than the values given may be detected. In unfavorable materials the given detectabilities may not be attained for some of the elements.

COMPARATIVE RESULTS

A comparison of chemical and microspectrochemical analyses of seven minerals is shown in Table 4.

The results provided by these techniques are visual estimates and should be given only a relative quantitative interpretation. Even under ideal conditions the brackets (10 to 3, 3 to 1, etc.) would overlap. Experience has shown that the judgment of the operator is important and his accuracy improves considerably with experience. When identifying a mineral, the information provided by these spectrographic techniques should be added to the *x*-ray diffraction data and (or) other chemical data before any final identification is made.

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The authors wish to express their appreciation to Robert Meyrowitz and Blanche L. Ingram for the chemical analyses, Daphne R. Ross for completing the *x*-ray studies, Katherine V. Hazel for making a few of the earlier plates, and Joseph F. Abell and Edward C. Curtis for altering the plateholder.

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MINERALOGICAL NOTE

Alice D. Weeks

The method of spectrographic analyses of very small samples (1 mg. or less) described in the preceding article by C. L. Waring and H. W. Worthing has been extremely useful in many mineralogical problems. The method has been used effectively in the study of uranium, thorium, rare earth and vanadium minerals, but is equally applicable to other mineralogical or chemical studies. The spectrographic analyses are especially helpful in the identification of minerals which are difficult or unsatisfactory to determine by optical properties or which do not give unique *x*-ray diffraction powder patterns; they are very useful for very small mineral samples or if there is a question in sampling to make sure that the *x*-ray pattern and the chemical constituents are determined on the same material. A few examples follow.

1) Distinguishing minerals that have similar *x*-ray powder patterns or checking minerals in which one element commonly substitutes for another. Metatorbernite $Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$ and metazeunerite $Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$ give similar *x*-ray patterns but the relative abundance of the phosphorus or arsenic anion can be checked spectrographically to give a satisfactory identification on a very small sample. An analysis also will check the presence of a significant amount of Ca, Ba, or various other elements that commonly substitute for the cation in the autunite and torbernite group of minerals. As with many hydration-sensitive minerals, the optical properties of the autunite-torbernite minerals vary with the hydration and commonly overlap from one species to another, resulting in inconclusive optical identification. The uranyl vanadates in some samples are difficult to distinguish with certainty from one another by optical properties either because of very fine grain size, hydration changes, or reaction with high index liquids. The distinctive cation can be checked spectrographically if necessary, on the *x*-ray spindle. This is particularly useful for the Ca and Ba in the metatyuyamunite ($Ca(UO_2)_2V_2O_8 \cdot 3\text{-}5H_2O$)-francevilleite ($Ba(UO_2)_2V_2O_8 \cdot 3\text{-}5H_2O$) pair which give very similar powder patterns.
2) Identification of small amounts of metamict minerals. This is often difficult because optical and *x*-ray determinations may be inconclusive. The spectrographic analysis may give the necessary additional data to complete the identification.
3) Very small samples or closely associated minerals which are difficult to distinguish and therefore present sampling problems. The sandstone-type uranium and vanadium deposits contain many fine-grained and closely associated minerals. It may not be possible to handpick enough pure mineral for many different tests or to tell by binocular examination whether thin coatings scattered on different parts of an ore sample are the same mineral. In the study of the Colorado Plateau samples in

the early 1950's the problem of sampling was critical as we were trying to accumulate data on new minerals and to untangle conflicting data on poorly defined or incorrectly described species. Abernathyite ($KUO_2AsO_4 \cdot 3H_2O$) is an example of a mineral that was recognized very quickly as a new mineral on the basis of a 1 mg. spectrographic analysis showing the presence of K, U, and As. Without the spectrographic check it would have been placed simply in the meta-autunite group.

4) Checking samples for *x*-ray powder pattern standard films. This is another use of the spectrographic analysis (if chemically analyzed material is not available) and it helped to build up a large set of reference *x*-ray films of minerals in our laboratory as quickly as possible.
5) Aid in microchemical analyses of small mineral samples. Spectrographic analyses of 1 mg. or less material have provided useful checks in testing residues or various steps in the chemical procedure when the sample was not large enough to make all the tests of a complete chemical analysis

In the past ten years the method of spectrochemical analysis of very small samples has served as a very effective exploratory technique before making time-consuming mineral separations and complete chemical analyses, as a check on other methods of identification, and as a source of useful semiquantitative data on composition.