USE OF ABSORPTION INTENSITY RATIOS FOR EMISSION SPECTROGRAPHIC ANALYSIS

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Consider a given spectral multiplet of an element. As the concentration of the element increases, a concentration will be reached at which the more intense component line of the multiplet will begin to self-absorb. With further concentration increases, the intensity ratios of that line to another weaker multiplet line will change with concentration and, hence, are a function of concentration.

It is shown that by proper control of the excitation process, the random behavior of self-absorption can be sufficiently reduced to allow the use of absorption intensity ratios for precise, accurate, quantitative determination of potassium.

Nearly all quantitative analytical applications of arc or spark emission spectography employ the internal standard principle introduced by Gerlach (6) in 1925. This concept refers the intensity of an emission line of the analysis element to the intensity of a line of the internal standard element which is present in constant concentration in both samples and calibration standards. Mathematically, the principle may be considered as follows:

The relative intensity, I_a, of a particular spectral line emitted by an element, A, is given by:

$$I_{a,\ n \rightarrow m} = N_a e^{-\Delta E_{n/kT}} g_n P_{n \rightarrow m} \gamma_a^4$$

where n and m denote the two energy levels involved in the transition producing the spectral line (n being a higher level than m), N_a is the number of atoms of A per unit volume of the excitation medium, $e^{-\Delta E_{n/kT}}$ is the Boltzman distribution term indicative of the relative populations of the excited states.

ΔE_n is the energy difference between the states n and m, k is the Boltzman constant, T is the absolute temperature, g_n is the

number of Zeeman levels the state n splits into in a strong magnetic field, P_{n-m} is the probability of a transition from the nth level to the mth level, and γ_a is the frequency of the line.

A similar equation describes the relative intensity of a line emitted by the internal standard element, S, arising from a transition between the r and q energy states of that element. Since the concentrations of the elements, C_a and C_s, are proportional to their respective numbers per unit volume, the intensity ratios of their respective lines can be obtained by:

$$\frac{I_{a,n\to m}}{I_{s,r\to Q}} = K_1 \frac{C_a e^{-\Delta E_n/kT} g_n P_{n\to m} \gamma 4_a}{C_s e^{-\Delta E_r/kT} G_r P_{r\to q} \gamma 4_s}$$

EQUATION II

$$\frac{I_{a,n\to m}}{I_{s,r\to q}} = K_2 \frac{C_a}{C_s} e^{(\Delta E_{r-} \Delta E_n)/kT}$$

EQUATION III

Where K_2 is a proportionality constant including all the constant terms in equation 2.

Two variables still remain; the ratio C_a/C_s and the temperature. If the excitation potentials (ΔE_r and ΔE_m) are equal, the Boltzman term vanishes and the fluctuation in temperature has little effect on the intensity ratios.

In practice, the internal standard method produces the best results when the following criteria are satisfied:

1. The line excitation potentials are matched.
2. The wave-lengths of the analysis and the internal standard lines should be nearly the same to compensate for lack of homogeneity in photographic emulsions.

3. The relative intensities of the lines should be similar to reduce potential calculation and/or densitiometry errors.
4. The volatilization behavior of the two elements should be alike.
5. The concentration of the internal standard element must be constant or known.

If these requirements can be reasonably well satisfied, the internal standard method gives compensation for variation in temperature and sample volatilization and for optical and photographic errors.

In 1944, J. Van Calker (13) suggested the utilization of the weakening of spectral lines by self-reversal in spectrochemical analysis. Since the weakening of a given line, in general, increases with the amount of the element present in the sample, empirical curves can be drawn relating the line attenuation to the concentration. As internal standard, it is possible to use a line, due to the element being analyzed for, which is relatively insensitive to self-reversal. In essence, this offers a method of "absolute" analysis since both the analysis and the internal standard lines are due to the same element. A few attempts have been made to apply this method (2, 3, 12) but their success was limited by a lack of control of the behavior of the absorbing "vapor" of atoms.

The potential advantages of this approach to quantitative spectrographic analysis are several:

1. The excitation potentials of the multiplet components are matched and their wave-lengths are often nearly the same.
2. Since the element is being used as its own internal standard, the method is potentially absolute, sample preparation is simplified, and sample volatilization behavior is of small consequence. Thus, it is reasonable to expect that an extended variety of sample types might be analyzed without observance of matrix effects or that matrix effects could be made negligible by the addition of an excess of a buffer element.
3. It is also likely that variations due to the use of different spectrographic facilities would be reduced if not rendered completely negligible.

Although this approach would not, generally, be applicable to trace element determinations, many elements exhibit multiplets which should allow self-absorption determinations over a wide concentration range (1, 9, 10). In short, this method takes maximum advantage of the internal standard principle, it is potentially universal with respect to sample type, it should be "absolute" in nature, and it should have significant analytical utility.

Since the original applications (2, 12, 13) of the method, several techniques have been developed that allow the imposition of greater control on the mode of excitation. On this basis it was determined to re-investigate the possibilities discussed above using modern excitation devices. Potassium, with doublet at 4044 and 4047 Å was chosen for the vital studies.

EXPERIMENTAL

Apparatus: A Bausch and Lomb Large Quartz Spectrograph, a National Spectrographic Laboratories multisource unit and a National Spectrographic Laboratories console model densitometer were used.

Preparation of Standards: Samples of known potassium composition were prepared by mixing potassium acid phthalate in a graphite matrix. Graphite was chosen primarily because it will act as a conductor as some of the samples to be analyzed consist principally of non-conducting oxides.

RESULTS

Moving plate and exposure variation studies were run to determine the extent of volatility effects. Figure 1 shows the moving plate data obtained using 10 second exposure intervals with 5 second

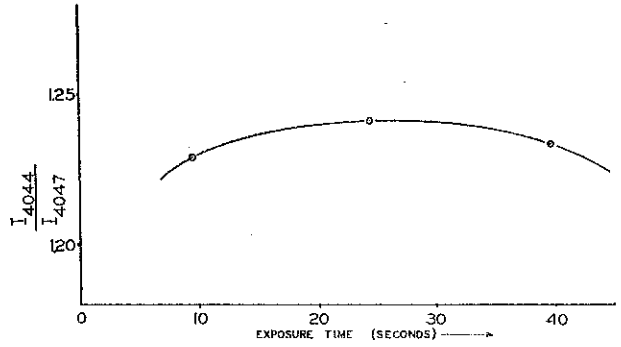

FIG. 1. MOVING PLATE STUDY

intervals in between. Note that the total intensity ratio change is less than 1.0% indicating a pronounced lack of volatility variation.

Figure 2 demonstrates the exposure time variation data for three individual determinations and again, indicates no volatility effects. The effects of varying the d.c. discharge current were also studied. Figure 3 represents typical data and indicates that maximum self-absorption, indicated by a decrease in the intensity ratio, occurs at a current of 9-10 amps. The possibility of increasing the degree of absorption and imposing more control on the absorbing vapor of atoms by using a Stallwood jet was also studied.

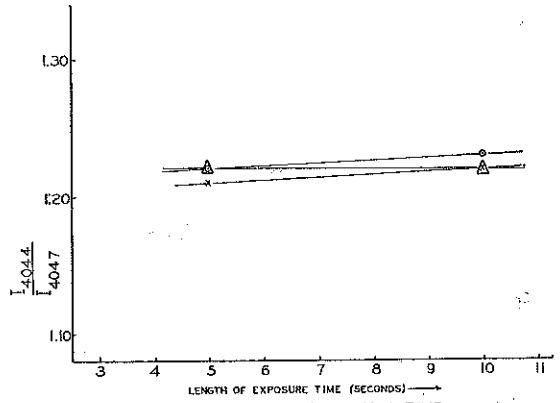

FIG. 2. INTENSITY RATIO vs. EXPOSURE TIME

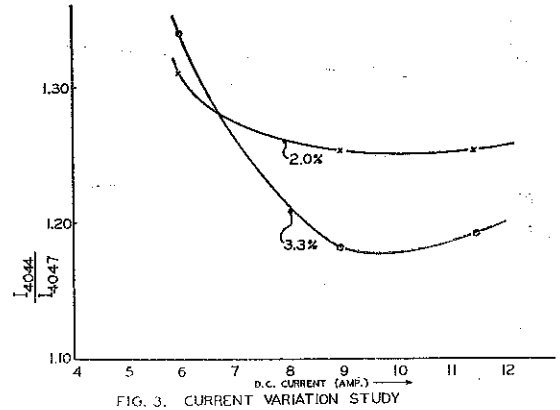

FIG. 3. CURRENT VARIATION STUDY

The Stallwood Jet consists of a hood which encloses the electrode discharge region and through which a gas steam is flushed. Since the principal escape route of the gas is through the window towards the spectrograph slit, the net effect should be an increase in the number of absorbing atoms along the optical path. An increase in the absorption controlling the flow rate of the gas should then offer a mode of control of the absorbing vapor. Figure 5 effectively demonstrates that this is true since we see an increase in absorption as the flow rate is increased. Note that the opposite is true when the restricting hood is removed.

Figure 6 shows that the ratio only changes within experimental error when the slit width is changed from 10 to 20 microns. On the basis of the studies made the conditions listed in Table I were chosen for the determination of potassium.

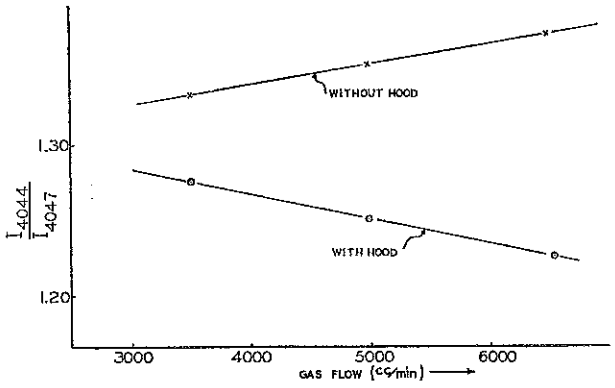

FIG. 5. ABSORPTION AS A FUNCTION OF GAS FLOW

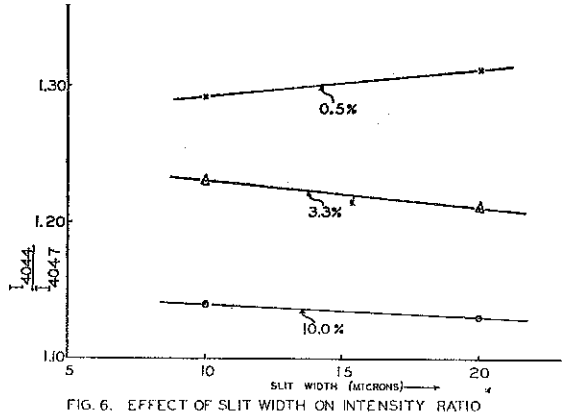

FIG. 6. EFFECT OF SLIT WIDTH ON INTENSITY RATIO

TABLE I
SPECTROGRAPHIC CONDITIONS

Weight of Sample	25 mg
Anode (Graphite)	(¼" diameter with sample cup 3/16" in diameter & ¼" deep)
Cathode (Graphite)	¼" diameter (60° point)
Argon Flow Rate	*9500* cc/min
Analytical Gap	4 mm
D. C. Arc Current	10 amps
Exposure Conditions	
Pre-Arc	10 seconds
Exposure	10 seconds
Plate Calibration	2 Step Density Filter Method
Slit Width	20 microns
Wave Length Range	3,400 to 5,000
Type Plate	Eastman Kodak SA3

Figure 7 shows the calibration curve prepared using these conditions and fitted by the method of least squares. The method can be utilized to determine potassium in the 0.5 to 10% concentration range. The 95% confidence limits for the curve are also shown.

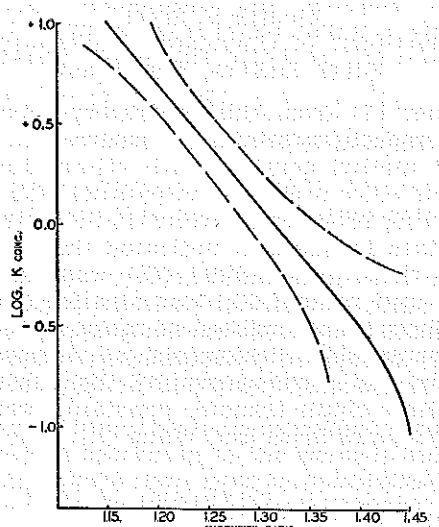

FIG. 7. INTENSITY RATIO vs LOG K CONC.

Thus, over most of the range, one can be 95% confident that the concentration determined is within ± 8% of the amount present.

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Correction of Telomer Chain Transfer Constant Data