THE SPARK-IN-FLAME METHOD OF SPECTROGRAPHIC ANALYSIS AND A STUDY OF THE MUTUAL EFFECTS OF ELEMENTS ON ONE ANOTHER'S EMISSION

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Introduction

In recent years the development of methods for the use of the spectrograph as an instrument for the quantitative as well as qualitative chemical determination of elements has proceeded to such an extent that they may now be regarded as suitable for application to many microchemical problems. While spectrographic methods cannot in general compete with ordinary chemical quantitative analysis in point of accuracy, they possess two important advantages which make them of great value in many special cases. These are great sensitivity, which permits of the semi-quantitative estimation of amounts of material too small to be analyzed by other methods, and the great rapidity with which an analysis can be conducted. For details of procedure, accuracy of estimation, etc., the reader is referred to the literature.

The three principal means of exciting emission spectra which have been used in quantitative analysis are the electric arc, the spark and the flame. The arc and spark methods combine the advantages of a high and to some extent controllable excitation with certain drawbacks. While the high

1 Original manuscript received August 19, 1931.
excitation makes the method applicable to a large number of elements, and
gives a great sensitivity, the difficulty of uniformly introducing representa-
tive samples of the material to be analyzed into the spark or arc gases, and
the fact that the emission of one element is not independent of the other
elements present, lead to some difficulties. These do not seem to be seri-
ous in the cases to which the arc and spark methods are usually applied,
that is, in the estimation of traces of impurity in a large and nearly con-
stant amount of some other substance, but they impose serious limitations
in case that all of the substances in the unknown samples vary largely in
relative amounts. The flame method, while very reproducible and nearly
free from the objections just cited, is limited in applicability to those few
elements which have relatively low excitation potentials.

**Purpose of the Investigation.**

It was the object of the work here described to devise a method
of spectroscopic analysis which would retain the advantage of the
flame method but overcome some of its limitations by allowing a
higher excitation. It was further proposed to study the mutual
effects of some elements on each other's emission with a view
toward finding conditions under which these are small, so that un-
known samples containing several elements might be analyzed with-
out extensive calibration experi-
ments.

**Description of Method and Apparatus**

**The Method.**--After some prelimi-
nary experiments the following method
was found promising. The difficulties
inherent in the ordinary spark methods
of vaporizing representative portions of
the sample to be analyzed were over-
come by atomizing solutions of the
sample into a hot flame, in the cus-
tomary way. The excitation in the resulting gases was then increased by passing
through them a condensed discharge.

**The Burner and Atomizer.**--Figure 1, which represents the burner and atomizer, is
self-explanatory. All parts were of Pyrex glass except the jet admitting gas into the
burner, which was of brass. The design was such as to yield a steady flame and to introduce as large a quantity of solution as possible into the flame gases in finely divided drops. Any large drops produced by the spray deposit on the walls of the atomizer vessel and run back quickly, reducing the volume of solution necessary for an analysis to about 3 cc.

The Spark.—The electrical circuit is shown in Fig. 2. The transformer finally used was a 2 k.v.a. American transformer operating on 220 volts and yielding 25,000 volts in the secondary. With this equipment an exposure time of one minute was usually sufficient. A smaller transformer gave nearly as good results with a longer exposure.

![Fig. 2.—Electrical circuit for production of spark-in-flame.](image)

The condenser consisted of 30.5 × 35.6 cm. plates of heavy window glass on both sides of which 25.4 × 30.5 cm. sheets of copper foil were cemented with shellac. Six plates were used and the capacity measured by a comparison method was found to be 0.013 microfarad. The inductance consisted of copper wire wound on three Pyrex glass cylinders covered with friction tape. The calculated inductance was 0.618 millihenris. With the combination of inductance and capacity given, the air lines were eliminated in the spark, and the intensity of the general background was not disturbing.

It will be noted in the diagram that an auxiliary spark gap and a fixed resistance were included in the secondary circuit. The former was found desirable since in its absence breakdown occurs at a very low potential due to the high conductivity of the flame gases. The latter serve to minimize variations due to changes in the conductivity of the flame when varying amounts of elements of low ionization potential were introduced into it, as shown in Table I.

### Table I

<table>
<thead>
<tr>
<th>Solution used for sample</th>
<th>Secondary current Without resistance wire</th>
<th>With 8' 4&quot; res. wire (54 ohms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>3.05</td>
<td>1.58</td>
</tr>
<tr>
<td>2 Molal NaCl</td>
<td>1.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The Flame.—The fuel in the flame was hydrogen gas saturated with acetone vapor, which gave a very stable flame little affected by the introduction of large amounts of foreign substances. The city gas available is a natural gas and was found quite unsuitable since it burns with a very unstable flame. It is probable, however, that most types of manufactured city gas would work satisfactorily without modification.

The Electrodes.—It was found possible in the following way to produce a spark which over a fairly wide region in its center was completely free from any lines due to the material of the electrodes. Tungsten electrodes 10–12 mm. apart were used, and these projected slightly into the flame from opposite sides. The tungsten vapor evolved is swept away by the flame gases and does not penetrate into the center of the flame. The spark was always passed just above the blue cone of the flame. Tungsten lines are apt to appear if the spark is too far above the cone. No improvement in sensitivity
was noted with closer electrodes, but tungsten lines appeared. The flame was made slightly "lean" in gas. The electrodes of the auxiliary spark were about 7 mm. apart.

Optical Arrangement.—A Bausch and Lomb quartz prism spectrograph was employed which has a dispersion of about 10 Å per millimeter at λ2800. The center of the spark was focused on the slit by means of a cylindric quartz lens, which was found to give a fairly uniform distribution of intensity over the entire slit.

Sensitivity and Excitation.—The excitation obtained under the conditions described above approximates what should be expected in a very high temperature flame. Lines of very high excitation potential which do appear in the spark are not obtained, but, on the other hand, many lines appear, especially at high concentrations, which are so weak in flames that they are not photographed under ordinary conditions. For example, Mg λ2796, Mg λ2802, and B λ2479 appear strongly, and fourteen lines of Na, Mg, Zn, Au, Cd and Tl have been identified which did not appear in the flame in comparison experiments and are absent in the acetylene flame spectrograms of Lundegårdh. The water and cyanogen bonds, of course, occur in the spectra obtained but on the whole the plates are cleaner and freer of background than those printed by Lundegårdh.

Photometry.—Since the purpose of the work outlined was to compare quantitatively the intensities of pairs of lines in the spark under various conditions, it was necessary to develop a method of rapid photometry. The intensities of two light sources are ordinarily compared photographically by cutting down one or both in a known way until the images which they produce on the photographic plate have the same density. This is most conveniently done by the use of rotating sectors, which are easily constructed and require no calibration. Calibration of wedges over a range of wave lengths is very laborious and screens could not be used in the present work.

The rotating sector has been condemned by some authorities because two effects, the "failure of the reciprocity law" and the "intermittency effect" may introduce large errors, but under certain conditions of operation these are found to counteract each other to a large extent, and within sufficient accuracy the intensities of two lines of the same density are inversely proportional to the sector opening. It is necessary that the sector speed be maintained above a certain minimum (120 r. p. m. is sufficient), that the plates used are not too "slow," and that the total exposure time be kept constant. For an intermittent source such as the electric spark, the time of a single opening of the sector should be large in comparison to the duration of the flash, and to the time between flashes.

A step sector wheel was constructed similar to that shown in Fig. 3 except that it had three times as many steps with the same total range of opening. Each opening is the cube root of two times the one below it, corresponding to a 26% increase of exposure, except for a correction which had to be made due to the fact that the cylindrical lens did not give a quite

3 (a) Weinland, J. Optical Soc. Am., 15, 337 (1927); (b) Weinland, ibid., 16, 295 (1928); (c) Weber, Ann. Physik, 45, 801 (1914); (d) Howe, Phys. Rev., 8, 674 (1916); (e) Newcomer, Science, 49, 241 (1910); (f) Rossler, Ber., 59, 2606 (1926); (g) Gibson and co-workers, Scientific Papers of the Bureau of Standards, No. 440 (1922).
uniform illumination over the entire slit. This sector was mounted as close as possible in front of the spectrograph slit and rotated at about 120 r. p. m. Every image of a spectral line of the plate then consists of a series of sections one above the other, of which the effective exposure increases logarithmically from the bottom to the top of the line.

If for a given spectral line the densities of the "sections" are plotted against the logarithms of the corresponding sector openings, a curve results whose shape depends on the characteristics of the plate and the development. Two spectral lines, sufficiently close so that the sensitivity and contrast of the plate are the same for both, will give curves of similar shape, but one will be displaced horizontally with respect to the other by an amount equal to the logarithm of the ratio of the intensities of the two lines in the source (see Fig. 4).

In practice, however, what one measures is an intensity due partly to the line emission of an element and partly to a continuous background which overlies the whole spectrum, and a correction must usually be made for the latter. It was found that where a sufficiently wide slit was used to permit of photometering the lines with an ordinary photoelectric photom-
eter, the blackening due to the background was such a large part of the total that the errors of measurement were very large.

However, it was found that the spectrograph slit could be narrowed sufficiently to make the density of the background negligible in comparison to that of the spectral lines, leaving the lines still sufficiently wide to be compared visually. When two lines were to be compared the photographic plate was cut between them, and the two portions brought into contact so that the two lines were side by side. One portion of plate was then moved up and down until opposite to one section of one line a section of the other line of equal density was found. If no exact correspondence could be found an interpolation was made. Knowing the sector openings corresponding to the sections chosen the relative intensities of the lines were easily estimated.

Two types of plates were used: Eastman D. C. Ortho with the ordinary Eastman D 61a developer, and Eastman "Regular" lantern slide plates with the contrast developer recommended. The former plates were developed for four minutes, the latter for two, stroking with a camel's hair brush, which gives exceptionally even development.

**Experimental Results and Discussion**

In order to make an estimate of the accuracy which might be expected of the analysis of simple solutions using the methods outlined, some intensity-concentration curves were first determined, as shown in Fig. 5. In each case the lines of the elements studied were compared with the copper line $\lambda 3247$, which was photographed by making each test solution 0.01 molal in copper nitrate. These curves should not be compared too rigorously with one another, since the plate sensitivity and contrast varies somewhat over the spectral region included.

The mutual effects which various elements have on each other's excitation were then studied. Since, as mentioned above, the atomizing of reasonable amounts of substances into a suitable flame did not appreciably change its temperature or volume, two principal effects remain to be considered. The introduction of substances of low ionization potential into the flame may be expected to change the conductivity and consequently the nature of the discharge and the excitation of all other elements present. Secondly, elements of low resonance potential when added may rob other elements of high excitation potential of their energy in collisions of the second kind, and cause their emission to be diminished.

A standard solution was prepared, 0.01 molal in copper, 0.01 molal in silver, 0.1 molal in thallium and 0.1 molal in cadmium, and the spark-in-flame spectrum of this was photographed beside the spectrum of another solution which was identical except for the addition of a rather large amount (1 molal) of a fifth element. In successive experiments this added element
### Table II

<table>
<thead>
<tr>
<th>Line</th>
<th>Exc. v.</th>
<th>Sodium Av.</th>
<th>Copper Av.</th>
<th>Silver Av.</th>
<th>Mercury Av.</th>
<th>Percentage change in intensity due to presence of 1 molal</th>
<th>Percentage error in analysis due to Na Cu Ag Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>3247 Cu 3.8</td>
<td>+26 +12 +26 +26 +26</td>
<td>+10 +10 +5 +5 +6</td>
<td>0 0 0</td>
<td>+25 .. +6 0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3274 Cu 3.8</td>
<td>+17 +12 +26 +28 +19</td>
<td>+7 +7 0 -5 +2</td>
<td>0 0 0</td>
<td>+20 .. +2 0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3281 Ag 3.7</td>
<td>+6 +4 +11 +14 +9</td>
<td>0 0 -2 -2 -1</td>
<td>+5 0 +3</td>
<td>+18 -2 .. +6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3384 Ag 3.6</td>
<td>0 0 +7 +9 +4 -3 -2 -3 -2 -3</td>
<td>+5 0 +3</td>
<td>+20 -15 .. +15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3775 Tl 3.27</td>
<td>+34 +26 +26 +26 +28 -3</td>
<td>0 +11 +3 +3 -3 -3 0 0 -2 0 0 0</td>
<td>+60 +6 -4 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3519 Tl 4.3</td>
<td>+51 +41 +68 +58 +54 -3</td>
<td>0 0 0 -1 +12 +12 0 0 +6 -5 -5</td>
<td>+90 -2 +10 -9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3261 Cd� 3.78</td>
<td>Decrease</td>
<td>Small decrease</td>
<td>0 0 0 0 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3610 Cd� 7.5</td>
<td>Decrease</td>
<td>Small decrease</td>
<td>0 0 0 0 0 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3460 Cd� 7.5</td>
<td>Decrease</td>
<td>Small decrease</td>
<td>0 0 0 0 0 0 0 0</td>
<td>2.1 3.8 3.6 4.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Resonance energy of element added (volts)  
* Cadmium lines were too weak to estimate accurately, but intensity change was small (less than 20%).
was varied, elements being chosen with widely different resonance and ionization potentials. The percentage changes in the intensities of certain copper, silver and thallium lines due to the addition of the “impurity” are given in Table II. The four determinations indicate the accuracy of the intensity comparisons.

![Diagram](image)

Fig. 5.—Intensity-concentration curves for several elements.

It will be noticed that the line intensities are usually increased by the “impurity” probably due to the increased conductivity of the flame gases. The last four columns of the table show the per cent. errors which these changes in intensity would cause in an analysis for copper, silver and thallium in case unknown solutions of approximately the same composition as those of the four solutions containing the “impurities” were compared directly with a test solution containing the three elements in the same concentration, but without the impurity. It will be seen that these errors are not larger than the average error of estimation except in the case of sodium.

**Conclusion**

One of the principal objects of the present work was to find conditions under which the spectroscopic analysis of solutions containing several elements in rather widely varying relative concentrations can be made rapidly...
without elaborate calibration experiments being necessary for each special case. Since under the conditions of the spark-in-flame the mutual effects of elements are in general not large, it appears that such analyses can be carried out with moderate precision if the intensities of the lines emitted by the unknown solutions are compared directly with the concentration intensity curves which have been determined once and for all on pure test solutions of the elements in which one is interested. In case alkali metals are present in high concentration their effect can be to a considerable extent allowed for by the addition, in known concentration, of a reference element absent in the unknown. This is the method of “Leitlinien” discussed by Lundegårdh.²

Summary

1. A new method of exciting spectra for the purpose of quantitative chemical analysis has been developed and studied. It consists in passing a condensed spark discharge through a flame into which is atomized a solution of the sample to be analyzed.

2. The excitation obtained, though less than that of the ordinary spark, is similar to that which should be expected in a flame of very high temperature, and many lines appear which are absent in ordinary flame spectra.

3. The mutual effects of some elements on each other’s emission in the spark-in-flame have been studied, and these have been found small enough to permit of a semi-quantitative analysis of unknown solutions containing several elements, without elaborate calibration experiments.

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