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INERT ATMOSPHERE EXCITATION:
A COMPLETE SPECTROGRAPHIC QUALITATIVE ANALYSIS SCHEME

by

Gloria Magliane Caton

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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Major Subject: Analytical Chemistry

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I. INTRODUCTION

Conventional qualitative spectrographic analyses are normally performed by vaporizing the sample from a carbon supporting electrode and exciting the spectra of the constituents by the same electrical discharge. Since the analyst is usually interested in recording as much information as possible, the dispersed spectra are usually photographed. The spectrograms obtained in this manner provide definitive information on the presence or absence of approximately 70 elements in the periodic system. It is of interest to note that most of these 70 elements have sensitive lines requiring less than 6 eV for excitation and that all of the sensitive lines of these elements are located in the visible wavelength region. The greatest deficiency of this analytical technique is that analytical information cannot normally be obtained for the following elements: oxygen, nitrogen, hydrogen, carbon, fluorine, chlorine, bromine, iodine, sulfur, and selenium. It is, of course, readily apparent why oxygen, nitrogen, carbon, and hydrogen bypass detection in the sample. These elements are major constituents of the gases (carbon vapor, constituents of normal air) which support the arc discharge. Even if they were not present as major constituents of the arc plasma, these elements together with fluorine, chlorine, bromine, iodine, sulfur, and selenium present another two-fold problem. First, Table 1 shows that the lowest excited states in the respective atomic energy level diagrams of these elements range from 6.3 up to 13 eV above the ground state. As a consequence, the sensitive resonance lines of these elements lie in the vacuum ultraviolet spectral region.

Table 1. Resonance lines

Element	Resonance lines	
	Wavelength (Å)	Excitation potential (eV)
F	954.8	13.0
Cl	1347.2	9.2
Br	1488.4	8.3
I	1830.4	6.8
S	1807.3	6.8
Se	1960.9	6.3
H	1215.7	10.2
N	1200.7	10.3
O	1302.2	9.5
C	1657.0	7.5

The second problem posed by these elements is that all the other line-producing transitions originate so high in the energy level scheme that the lines are weak in intensity. The atomic energy level diagrams of fluorine and iodine, shown in Figure 1, illustrate this problem very well. Transfer of over 8 eV during inelastic collisions would be required to cause emission of any of the non-resonance lines of these elements. For iodine, approximately 8.3 eV would be required to cause emission of lines in the conventional photographic region of the spectrum while for fluorine, 14.4 eV is necessary.

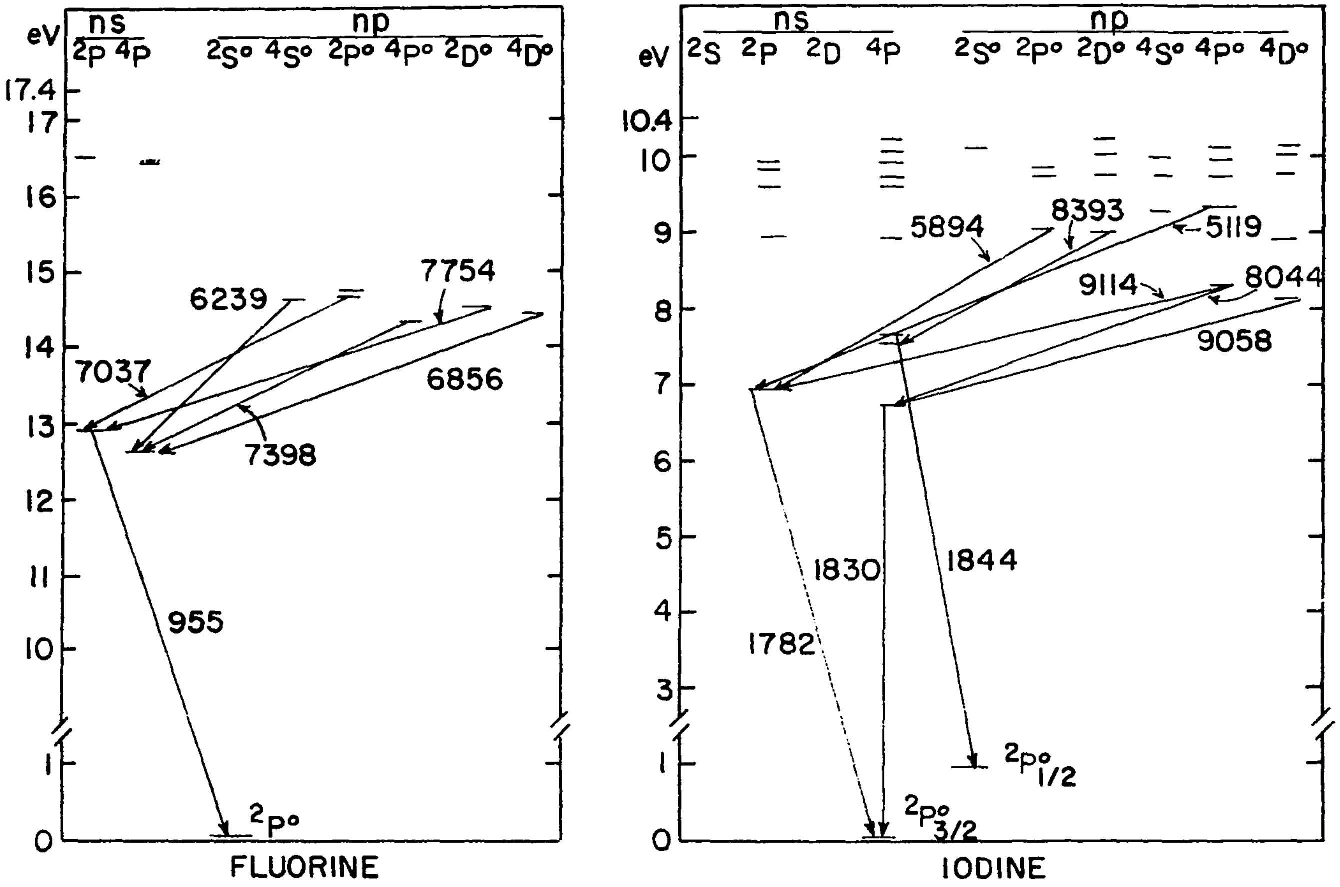


Figure 1. Simplified atomic energy level diagrams. Wavelengths expressed in Å

An examination of the energy distribution in a d.c. carbon arc plasma reveals why it is so difficult to populate excited states which are located so far above the ground state. There is general agreement (15,87,93) that local thermodynamic equilibrium (LTE) prevails in d.c. arc discharges at atmospheric pressure. When LTE exists, it is then possible to describe locally the distribution of energies of the particles in the discharge column by the Maxwell-Boltzmann distribution law (110).

$$\frac{dN}{N} = 2\pi\left[\frac{1}{\pi kT}\right]^{3/2} E^{\frac{1}{2}} \exp(-E/kT)\ dE$$

where $\frac{dN}{N}$ - fraction of particles possessing an energy between E and E + dE

E - kinetic energy

T - temperature (^{o}K)

k - Boltzmann constant.

This equilibrium energy distribution is dependent only on the absolute temperature and therefore any volume of particles in a discharge column that are in LTE can be described by some temperature. If, for example, an average temperature of a d.c. carbon arc is assumed to be approximately 8000^{o}K (100), the energy distribution shown in Figure 2 exists. The corresponding average energy of the particles at this temperature (3/2 kT) is only about 1 eV. Thus, only collisions with the very small number of particles in the high energy "tail" of

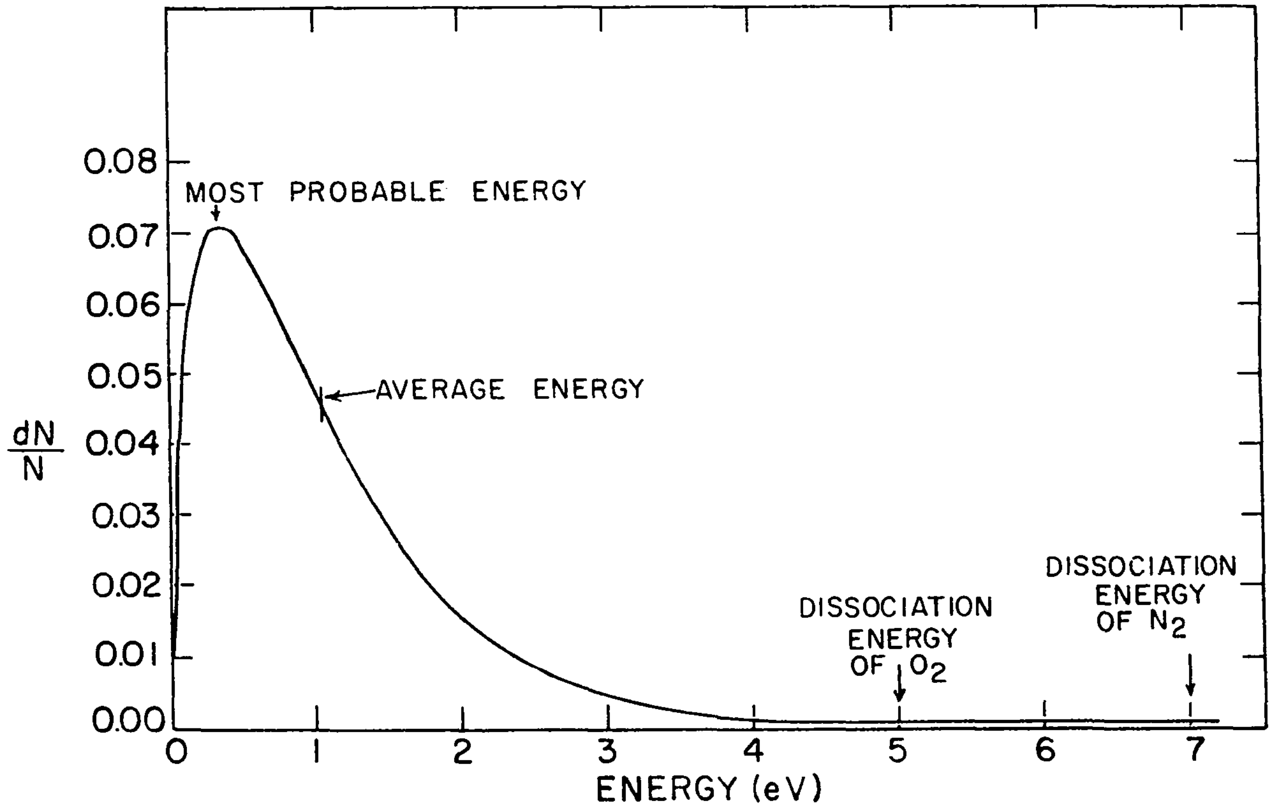


Figure 2. Maxwell-Boltzmann energy distribution curve for T = 8000°K

the Maxwell-Boltzmann distribution curve play an important role in populating the higher energy states in elements such as chlorine.

II. PURPOSE OF RESEARCH

The goal of this research was the establishment of a practical qualitative spectrographic analysis scheme which would include the detection of as many elements in the periodic table as possible. In addition to the elements generally included in such qualitative schemes, the object of this research was to incorporate the halogens, sulfur, selenium, and, if possible, oxygen, nitrogen, hydrogen, and carbon into a general and practical qualitative analysis scheme. To be useful and practical such a scheme must meet certain overall requirements. The procedure should provide acceptable detection limits for the halogens, sulfur, selenium, oxygen, nitrogen, carbon, and hydrogen, as well as for the remainder of the elements in the periodic system. The scheme should not require the use of special excitation sources, i.e., commonly available commercial excitation sources should be adaptable. The excitation scheme should not be unnecessarily elaborate; preferably, in each wavelength region a single exposure should suffice for the detection of all the elements. Conventional spectrographs and photographic emulsions or films should be adequate for the recording of the spectra. The excitation scheme employed should be directly applicable to solid samples that are electrically conducting or nonconducting. Prior dissolution of the sample should not be required.

In achieving the above goals and requirements, it was convenient to divide the total problem into two major parts. First, an acceptably sensitive technique would be developed for the excitation of the emission spectra of the halogens, sulfur, selenium, and if possible, oxygen, nitrogen, hydrogen, and carbon. Second, the effectiveness of the technique devised for the excitation of the "difficult-to-detect" elements would be evaluated for the qualitative detection of other elements in the periodic system.

III. HISTORICAL

Characteristic spectra useful for qualitative detection of the elements oxygen, nitrogen, carbon, hydrogen, chlorine, bromine, iodine, fluorine, sulfur, and selenium have been observed under a variety of experimental conditions. The question then arises whether the excitation and observational schemes employed can be incorporated into an experimental system which may be useful for performing practical qualitative analyses. To answer this question, a rather comprehensive compilation of prior reports on the analytical observations of the halogens and sulfur, as representative elements, was undertaken.

A. Characteristic Band Emission Spectra

In the hot environment of conventional flames and d.c. or a.c. arc discharges, it is possible to form diatomic molecular emitters of the halogens. The most useful of these emitters are the alkaline earth halides in arc discharges and in flames (5,19,33,42,47,49,62,88,101,103,109) and copper chloride in flames (44). The latter forms the basis of the well known Beilstein chloride flame test. Among the band systems which have been employed for the qualitative detection or quantitative determinations of the halogens, the bandheads of calcium fluoride at 5291 and 6064 Å, (5,14,33,47,49,88,101,103,109), strontium fluoride at 5772 Å (19), and calcium chloride at

6211 and 5934 Å (5,47) have been found most useful. Only weak emission of doubtful analytical utility has been observed from the respective bromide and iodide molecules (5,47). An excess of calcium atoms must be present in the flame or arc plasmas for the efficient formation of the diatomic molecules. This requirement detracts considerably from the qualitative analysis utility of these spectra, because the addition of calcium precludes the identification of this element in the original sample.

B. Characteristic Line Emission Spectra

1. D.c. arc discharges

Line spectra of the halogens have also been excited with a d.c. arc discharge. Reinold and Schroll (92) excited a low-energy atomic iodine line (7 eV) with a d.c. arc discharge in air. Using this 2062 Å line, these investigators detected 0.002% iodine in the complete absence of alkali salts.

By replacing air with a noble gas supporting atmosphere, other workers were able to photograph the characteristic high-energy lines of the halogens found in the visible region. Vilnat *et al.* (114,115,116) devised a "blowing" electrode and a "double injector" system, both of which enabled the arc discharge to be maintained in a helium atmosphere without the utilization of an enclosed chamber. With this arrangement, they were able to obtain spectra of the high-energy atom and ion lines of the halogens, sulfur, and selenium when these elements were present as major constituents.

After dilute solutions containing the halogens and sulfur were evaporated into a graphite electrode, Tveekrem (113) found that these elements were efficiently excited in a d.c. arc only when the sample electrode was the cathode and the supporting atmosphere was helium or neon. The optimum line intensities of the halogens and sulfur were obtained at a pressure of 200 Torr. It is logical that the most efficient excitation should occur at the cathode because the cathode fall region of a d.c. arc is characterized by energies comparable to the ionization potential of the supporting atmosphere (43). Thus for the noble gases, krypton, argon, neon, and helium, energies of approximately 14 to 24.5 eV would be found in the cathode fall region. In other probing experiments in which a sample consisting of 1.5% of each of the halogens and sulfur in a magnesium oxide matrix was arced in a helium supporting atmosphere, Tveekrem was unable to detect any lines of the halogens and sulfur.

The successful detection of the halogens and sulfur in d.c. arc discharges supported by the noble gases can be readily interpreted. The excitation in a d.c. arc is accomplished predominantly by inelastic collisions of electrons with atoms and molecules. The number of available high energy electrons in an electrical discharge of this type is influenced by the supporting atmosphere. In an atmosphere containing a large number of molecular species, the electrons have a high probability for inelastic collisions with these molecules when the electronic energy exceeds the energy necessary for the excitation, dissociation, or ionization of the molecular species. Likewise, in atmospheres composed of atomic species there is a large probability for inelastic collisions between electrons and atoms when the electronic energy surpasses the amount of energy needed for the excitation or ionization of the atoms. The electrons will lose a large portion of their kinetic energy in these inelastic collisions and therefore the excitation characteristics of the supporting atmosphere will tend to limit the maximum energy available in the discharge for the excitation of the analyte elements. For example, in an air atmosphere the maximum energy available for excitation is primarily limited by the dissociation energies of oxygen and nitrogen, namely 5 and 7 eV, respectively. This means that there will be very few electrons which have energies in excess of about 7 eV in an air atmosphere.

The maximum energies available in arc discharges supported by monoatomic noble gases are determined by the excitation and ionization potential of the particular gas. Of these two processes, ionization is more important than excitation (41). Thus in an argon supporting atmosphere, not many electrons would be expected to have energies in excess of 16 eV because the lowest excitation energy of argon atoms is 11.6 eV and the ionization potential is 15.8 eV. The lowest excitation potential and the ionization potential of helium are considerably higher, 19.8 and 24.6 eV, respectively, and therefore an electrical discharge in a helium atmosphere would be expected to produce excitation of much higher energy levels.

Of the previous investigators, Vilnat _et al_. were able to obtain spectra of the halogens when these elements were present as the major constituents in samples. Tveekrem detected lines of the halogens only when his sample consisted of dilute solutions of the halogens which were evaporated on a graphite electrode. It is evident that both of these methods are impractical for a general qualitative analysis procedure. The results of the preceding investigators have indicated that the extension of the d.c. arc method to the analysis of trace amounts of the halogens in some matrix has thus far not been found feasible.

2. Conventional high-voltage condensor discharges

a. _Solid samples_ With a spark discharge in air, background radiation limits the analytical usefulness of several wavelength regions. Nevertheless, Johnson and Norman (50) have detected 0.1% fluorine and 0.07% iodine in finely divided samples held in a cored graphite electrode. To accomplish this, they utilized a conventional spark source in an air supporting atmosphere. However, they had to pass carbon dioxide through the discharge column during the analysis for chlorine and bromine in order to eliminate interferences from air lines. Several other authors have avoided the limitations imposed by an air supporting atmosphere and simultaneously increased the available energy for excitation by utilizing gases other than air (usually the noble gases) for the supporting atmosphere.

Mansfield, Fuhrmeister, and Fry (70) reported an increase in line intensity of the halogens and sulfur and a decrease in the intensity of the background radiation when they changed the supporting atmosphere from air to helium. However, when Gunn (35) replaced air in the discharge column with a stream of helium, he found a reduction in the intensity of chlorine and sulfur lines and the background. Gunn indicated that the difference between his and Mansfield's results was probably due to different excitation conditions. Both Gunn and Mansfield _et_ _al_. sparked their samples in a fabricated silver pellet opposite a silver counterelectrode. Hurd (46) also found that the background intensity decreased when helium was passed across the analytical gap. In addition, Hurd noted an increase in background when an air atmosphere was replaced by argon. Using a helium atmosphere, Hurd detected 0.5% sulfur in a sample mixed with graphite and formed into a conducting rotating disc.

Whereas Johnson and Norman, Mansfield, and Gunn simply enveloped the spark plasma with noble gases, Harvey and Mellichamp (39) utilized an atmospheric control system for their excitation chamber. With this arrangement Harvey and Mellichamp also were able to observe spectra emitted in spark discharges at reduced pressures. They indicated that pressures between 10 and 40 Torr were the most satisfactory. When samples were excited in both air and argon at 20 Torr, Harvey and Mellichamp noted no great difference between these gases although the sensitivities were generally better in argon. Utilizing a conventional high-voltage spark source similar to the previous authors', a silver sample electrode and counter-electrode system, and an argon atmosphere at a pressure of 20 Torr, Harvey and Mellichamp detected 0.1% carbon, 0.05% phosphorus, 0.07% sulfur, 0.01% chlorine, 0.1% selenium, 0.01% bromine, and 0.03% iodine. However, it is important to note that they were unable to detect 5% fluorine. One reason for this might be that their observations were apparently restricted to the 3500 to 5000 Å region and the sensitive fluorine atom line is located at 6856 Å. The paper does not indicate what fluorine lines they were considering.

Using a high-voltage spark superimposed on a 29 A d.c. arc in an argon atmosphere at 75 Torr, Contamin (20) detected 0.005% chlorine in graphite pellets. However, with the same experimental conditions he was only able to see faintly 10% fluorine. After experimenting with different pressures in argon, an argon and helium mixture, helium, and neon, Contamin finally detected 0.05% fluorine in a silver pellet utilizing different electrical conditions in a neon supporting atmosphere at 400 Torr. It is evident that Contamin's method is not very practical especially when more than one element must be determined in a given sample.

Thus, several different investigators have reported considerable success in detecting the halogens by employing high-voltage spark discharges in noble gas atmospheres at reduced pressures. Pressure is an important variable because it influences both the vaporization and excitation of the sample material. In a spark discharge, sample vaporization is caused by positive ion bombardment of the cathode (see Chapter IV). The total number of ions in the discharge column increases as the pressure increases, but the energy that the ions acquire increases with decreasing pressure because the number of collisions in which the ions participate decreases. Inelastic collisions of electrons with sample atoms are the principal excitation mechanism in a spark discharge. With decreasing pressure the electrons acquire longer mean free paths, are able to attain higher energies, and should be more efficient in populating excited states of high energy. However, there is no a priori reason to suppose that the most efficient sample vaporization will occur at the same low pressures where the excitation process is most probable.

The vaporization (sputtering) efficiency in an argon atmosphere is high because of the heavy mass of the argon ions. As a result of the high probability for inelastic collisions between electrons that possess energies equal or greater than 12 eV and argon atoms, the discharge should be maintained at low pressures in order for the electrons to most effectively populate high-lying energy levels. Indeed, Harvey and Mellichamp and Contamin most successfully detected the halogens when they utilized low pressures in argon atmospheres.

The excitation of the high-energy lines of the halogens is more probable in neon and helium than in argon because the energy distribution of the electrons is shifted to higher energies in neon and still higher energies in helium. However, helium ions are light and therefore not as effective as neon and argon ions in vaporizing the samples. Nevertheless, in a helium atmosphere, the probability for the excitation of any vaporized sample material is high.

Pressure and the nature of the supporting gas also exert an influence on the background radiation. Bremsstrahlung, i.e., free-free transitions, (8,23,86,102) and ion-electron recombination (23,102) processes have been proposed as explanations for the occurrence of continuous radiation at different stages of a spark discharge. Because the probability for the preceding processes, and consequently for background continua, increases with increasing ion concentration, more background radiation would be expected at high pressures and in supporting atmospheres that have low ionization potentials. Consequently, the substitution of helium for air should result in a decrease in the intensity of the background radiation which indeed was observed by several investigators (35,46,70).

In summary, it is clear that prior investigators were successful in achieving reasonably good detection limits for the halogens when conventional spark excitation was performed in noble gas atmospheres. However, the detection limits thus far attained leave much room for improvement.

b. Liquid samples Several authors have analyzed solutions (55,56,60,91) and solution residues (28,29,111,124) for the halogens with conventional spark discharges. Using an ignited low-voltage spark between a copper rotating disc and counterelectrode, Kibisov (55) detected 0.001% sulfur, 0.001% iodine, 0.01% bromine, and 0.01% chlorine in separate samples. However, because Kibisov used different values of self-inductance for the analysis of each element the general application of his method would be difficult. Kudymov, Malinina, and Varlamov (60) detected 0.005% chlorine, 0.005% sulfur, 0.01% bromine, and 0.01% iodine by sparking aqueous solutions with the aid of a fulgurator and carbon electrode. The fulgurator had a volume of 1 cm^3 and consisted of a carbon electrode positioned in the center of a glass vessel that held the sample solutions. A 0.8 mm capillary channel passed through the carbon electrode. A thin film of solution formed on the top of the carbon electrode by capillary action and was continuously replenished during the sparking.

In another solution method, chlorine (0.00001%) in rainwater was detected when the sample was evaporated to a tenth of the original volume, placed in an iron electrode, and sparked (124). It should be noted that the detection limits for these solution methods are not as attractive as they seem. They are based on the weight of the unknown element relative to the weight of the solution instead of being based on the weight of the unknown element relative to the weight of the original solid sample. For example, if a 0.5 ml aliquot of a 1% solution, i.e., 0.005 gm of sample material present in this 0.5 ml volume, was consumed in the course of the exposure, then a reported detection limit of 0.001% in solution would correspond to a detection limit of 0.1%, [(0.000005 gm detected in a 0.5 ml aliquot/0.005 gm sample)x100], in the actual matrix. Thus if a 1% solution was used, practical detection limits with reference to the matrix material would be decreased by a factor of 100.

Analysis for the halogens was also accomplished by the copper-spark method, which consists of evaporating dilute sample solutions on copper electrodes and then sparking the electrodes. Using this method, Fizalkowski <u>et</u> <u>al</u>. (28,29) found 0.05% fluorine, 0.01% chlorine, 0.001% bromine and

0.001% iodine in solution. Taylor and Webb (111) detected 0.0005% selenium, 0.01% fluorine, 0.001% bromine, 0.001% iodine, 0.001% chlorine, and 0.001% sulfur in separate dilute solutions. The sample solutions analyzed contained negligible quantities of matrix analyte and consisted of dilute (1% or lower) aqueous solutions of individual alkali halide salts. In several cases the intensity of the impurity lines was suppressed by the presence of species other than the test element in the sample (85,111,121). The amount of residue deposited on the copper electrodes was another critical factor in this method. Residue in excess of 1 mg formed a flaky crust which was easily dislodged by the force of the discharge in the first stages of sparking.

Although good powers of detection have been observed for the techniques discussed above, prior dissolution of the sample is required in all cases, and preliminary chemical separations in some. Both of these steps are impractical in a qualitative analysis scheme of general utility. Consequently these techniques were not seriously considered in further evaluations.

3. Specially designed discharges

Specially designed light sources characterized by high current densities and consisting mainly of modified a.c. arc circuits (107,108) have been used for the detection of the halogens and sulfur. Sources included in this classification are the low-voltage sparks (57,89,90), "Hot Arc" (63,64), and square wave pulse generator (117).

Working at pressures of 2 to 20 Torr, Pfeilsticker (89, 90) obtained strong lines of the halogens and sulfur with an ignited low-voltage spark source of high current density. Peak currents of about 780 A resulted during the discharge of the 400 to 2000 μf condenser, previously charged with 220 to 300 V. Pfeilsticker indicated that he was able to obtain the spark lines of the nonmetals owing to the high current density, reduced pressures, and short spark durations (10^{-4}sec) characteristic of his source arrangement.

In the "Hot Arc" source used by Levintov (63,64), the sample was vaporized by an arc discharge and the sample vapor was excited by a periodic discharge of a 6000V, 1μf condensor through the arc. The slit to the spectrograph was opened only during the pulse discharge. Bromine and sulfur spectra were observed with this arrangement.

Huang (45) devised a source consisting of two arc circuits connected in parallel so that each could be regulated separately. A graphite crucible containing the sample was placed between two electrodes and was heated by the lower arc. The upper arc, adjusted so that the resulting discharge might vary from an arc to a spark, excited the sample. The detection limit for bromine and chlorine in copper oxide samples was 0.03%.

With a vacuum condensed spark, Balloffet et al. (6,7,94, 95) detected 0.03% bromine, 0.01% selenium, 0.005% sulfur, and 0.005% phosphorus in the far ultraviolet spectral region. It should be pointed out that many experimental difficulties are encountered in this wavelength region. The absorption of radiation by atmospheric constituents below 1950 Å and by quartz at or below 1850 Å necessitates the enclosure of the spectrograph and the source in a vacuum tight case. A good evacuating system, special optics, and specially prepared photographic plates are also necessary for work in this wavelength region (38,98).

A common disadvantage of the sources considered in this section is that they are specially designed and therefore not commercially available. Consequently the discussion of these sources was included only for completeness and they have been omitted from further consideration.

4. Hollow cathode discharges

Exceptionally good detection limits for sulfur and the halogens have been observed by hollow cathode excitation. The reported detection limits were in the range of 0.01 to 0.0001% for fluorine, 0.01 to 0.001% for chlorine, 0.05 to 0.005% for bromine, and 0.03 to 0.001% for iodine and sulfur. All types of samples have been analyzed. Solid samples have been deposited or fused inside a hollow cathode (26,58,59) and powders (4,10,11,12,13,18,32,67,77,79,80) or solutions (9,81) have been deposited or evaporated on the inside surface of the cathode. It is also possible to fabricate the hollow cathode out of a conducting sample. The ideal sample form was a thin, uniform film spread over the inside of the cathode. A typical sample weight ranged from 10 to 60 mg. Birks (13) found that sample weights greater than 100 mg were undesirable because of the resulting distortion of the discharge and the incomplete sputtering of impurities. Helium at pressures of 2 to 15 Torr was normally selected as the carrier gas in the hollow cathode although argon and other gases could also be used.

The presence of alkali or alkaline earth elements has been found to decrease the intensity of the higher energy nonmetal lines. Berezin and Yanovskaya (12) found that 0.1 to 5% sodium gradually decreased the intensity of the iodine lines. Quantities of the alkali or alkaline earth elements greater than 0.03% resulted in the understating of the chlorine and fluorine concentrations in Korovin's work (58). In contrast Birks (13) found that a twenty-fold excess of sodium and of chlorine exerted no appreciable suppression of 25 μg of fluorine.

A disadvantage of the hollow cathode discharge was the loading and evacuating required for each sample. However, Berezin (9) used a specially designed molybdenum glass tube in which six hollow cathodes could be loaded simultaneously.

In summary, it is evident that the use of hollow cathode discharges for the detection of the halogens and sulfur has been quite successful.

5. High-frequency discharges

Spectra of the halogens may also be obtained when samples are volatilized and excited in electrodeless, high-frequency discharge tubes, operated at low pressures (31,54,97,99,119, 120). Because of the low thermal power of the electrodeless, high-frequency discharge, this source was limited to the analysis of gases or easily volatilized solid samples (78).

Halogen detection was suppressed by a factor of ten or greater in samples containing nitrates or carbonates. A considerable part of the available energy apparently was used in the excitation of band spectra of the evolved gases. The band spectra increased the spectral background and masked the analysis lines (31).

Because of the lack of reproducible sample vaporization, Keller and Smith (54) reported that quantitative analysis using an internal standard was not practical with high melting inorganic salts such as the alkali halides. Reproducibility was difficult to achieve because of varying pressure and temperature in the discharge tube.

Because of its sample limitations, the high-frequency discharge method has been discussed above only for purposes of completeness.

6. Sensitive lines of the halogens

One of the purposes of the undertaking of the rather comprehensive survey of the literature with respect to the spectroscopic detection of the halogens was the compilation of a list of analytical lines of these elements. This compilation is found in Table 2.

7. Summary

In summary, a detailed investigation of the literature for excitation sources suitable for the routine analysis of the nonmetals indicated that either spark discharges in a noble gas atmosphere or hollow cathode discharges would offer the best promise for success. However, because of the necessity of making a choice, the spark discharge was selected because the sample preparation for this method was deemed easier. It is now of interest to examine the nature of the energetic spark discharges and get some insight as to why these excitation sources offer great possibilities of detecting the halogens.

Table 2. Analytical lines of the halogens and sulfur

Wavelength (Å)	Excitation potential (eV)	References
		Fluorine
3503.1 II	(28.5)	29,70,111
3505.6 II	(28.5)	20,29,70,111
3847.1 II	(25.0)	20,70
6239.6 I	14.6	14,115
6856.0 I	14.4	4,13,14,20,26,31,50,58,59,67,91,113,115
6902.5 I	14.5	13,31,50,91
6909.8 I	14.5	26
7037.4 I	14.7	9,10,18,26,31
7128.0 I	14.7	13,58,59
7202.4 I	14.7	13
7398.7 I	14.3	4,13
7425.6 I	14.3	4
		Chlorine
3191.4 III	25.4	29,55,111
3340.4 III	25.2	29,111
3602.1 III	25.0	35,70
3612.8 III	24.9	35
3622.7 III	24.8	35
3827.6 II	21.4	115
3851.5 II	19.1	26,55
4794.5 II	15.9	9,10,13,14,18,31,39,50,58,60,64,70,90,91,113,119,124
4810.1 II	15.9	13,14,18,31,39,45,50,64,70,90,91,97,119
4819.5 II	15.9	31,39,45,50,56,64,70,91,119,124
4904.8 II	18.2	56,91
4917.7 II	18.2	56
5078.2 II	18.1	56
7414.1 I	10.6	4
8376.0 I	10.4	20

Table 2. (Continued)

Wavelength (Å)	Excitation potential (eV)	References
		Bromine
2389.7		55
2926.3		14,29,55,111
3506.5		35,70
3562.4		14,29,111
4678.7		14,50,56
4704.9 II	14.3	14,31,39,50,60,70,90,91,115
4785.5 II	14.2	13,31,39,45,50,56,70,90,91,113
4816.7 II		9,39,50,56,70,97
5332.0		91
7005.2 I	9.8	4
7348.6 I	9.7	4
7425.9 I	10.9	4
8272.5 I	9.4	13
		Iodine
3055.4 II	18.3	29,55,111
3078.8 II		29
3498.0		70
3724.8		70
3897.3		70
3940.2		55
4409.0 II	15.2	115
4452.9 II	14.8	39
4512.6		39,70
4666.5 II	14.8	39
4808.0		13
4986.9		13
5161.2 II	12.4	14,31,50,60,90,91
5245.7 II		91
5338.2 II	13.9	12,113
5405.1/7		14,31
5407.4 II		9,12
5464.6	12.3	14,31,50,90,91

Table 2. (Continued)

Wavelength (Å)	Excitation potential (eV)	References
		Sulfur
2863.5		14,111
3497.3 III		35,70,111
3838.3 III	21.4	55
3993.5 II	17.3	115
4028.8 II	18.9	115
4142.3 II	18.8	70
4145.1 II	18.8	70
4153.1 II	18.8	70
4162.7 II	18.8	39,70
4174.3 II		70
5032.4 II	16.1	31,91
5432.8 II	15.8	89,91
5453.8 II	15.9	9,10,31,46,57,60,64,89,90,91,113
5640.0 II	16.2	57,89,91
6305.5 II	16.1	4
6312.7 II	16.1	4,18

IV. A HIGH-VOLTAGE SPARK DISCHARGE

A representative circuit for a typical controlled high-voltage spark source is found in Figure 3. The transformer typically has a peak voltage output of 15,000 to 40,000 V. The condenser (C) could be charged to these voltages during each half-cycle, if the breakdown of the control and analytical gaps did not occur during this charging cycle.

The control gap is inserted into the circuit to regulate the voltage at which the discharge occurs. This is to ensure that the energy stored in the condenser ($\frac{1}{2}CV^2$) and dissipated in the gap is precisely reproduced for each discharge.

The spacing of the control gap is maintained at a separation greater than that of the analytical gap and consequently determines the actual voltage at which the condenser will discharge. The breakdown potential is not influenced in any manner by the analytical gap. A typical spacing for the control gap is about five mm when the spacing of the analytical gap is maintained at four mm or less. Because the control gap has a higher resistance than the analytical gap, current cannot flow in the circuit until the breakdown of the control gap occurs. A high velocity stream of air, blown across the control gap, rapidly quenches each spark train and deionizes the gap. In this manner, conditions in the control gap are reproduced from half-cycle to half-cycle. The extinction of the discharge and removal of ions enables the control gap to

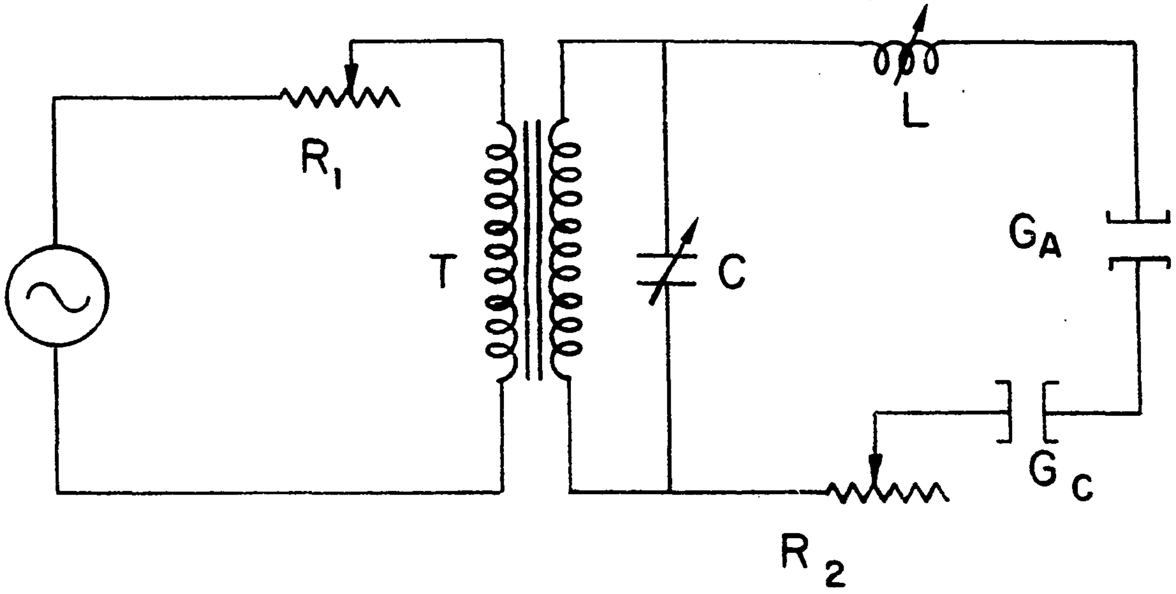


Figure 3. Circuit for a high-voltage spark. Resistor R_1 is a current control; T is a high-voltage transformer; resistor R_2, inductance L, and capacitor C control the electrical characteristics of the spark; G_A is the analytical gap; and the control gap is G_C

break down several times in a half-cycle, if desired. Deionization of the control gap is not sufficient to produce precise breakdown voltages. Variable oxidation of control gap electrodes may also introduce erratic breakdown voltages. This problem is corrected by irradiating the control gap with ultraviolet light, thus producing a definite ion density in the gap before the next condenser discharge occurs. In this manner the condition of the gap is reproducible and a constant breakdown voltage is obtained for each discharge.

Spark sources based on the auxiliary air-control gap are described in greater detail by Enns and Wolfe (24,25) and Fowler and Wolfe (30). Descriptions of other controlled spark excitation sources and modern excitation units are given by Jarrell (48).

When the breakdown potential of the control gap is achieved, the condenser discharges through the resistance and inductance of the discharge circuit in addition to discharging through the gaps. Thus, the form of the discharge current and voltage pulse is influenced by the values of the resistance, inductance, and capacitance in the discharge circuit.

If the amount of resistance in the discharge circuit is small ($R^2/4L^2 < 1/LC$), then at each breakdown of the gap the current flows back and forth through the discharge circuit as a damped oscillatory discharge. This oscillatory discharge has a frequency approximately equal to $1/2\pi(LC)^{\frac{1}{2}}$. In a typical high-voltage spark, the frequency is about 10^6 cycles per second. The current oscillations are damped because of the energy dissipated in the gaps as well as in the circuit. When the gap resistance is neglected the current passing through the gap is given by the equation,

$$i = [V(C/L)^{\frac{1}{2}}]\,[\exp(-Rt/2L)]\,[\sin(1/LC)^{\frac{1}{2}}t]$$

V is the voltage to which the condenser is charged at the time of breakdown and t is the time after the gap breakdown. The peak current for low damping is approximated by the first term in the above equation. The second term in the equation expresses the damping and the third represents the oscillations. The initial peak current may be several hundred amperes, which rapidly drops to an average current of a few amperes. If more resistance is added to the circuit so that $R^2/4L^2 = 1/LC$, the circuit is critically damped and no more oscillations occur. For the case, $R^2/4L^2 > 1/LC$, the circuit is overdamped and arc-like (40).

The choice of electrical parameters influences the nature of the resulting discharge. A more energetic spark is obtained when the inductance (L) in the circuit is reduced. This reduction in L causes the current to increase and the period of oscillations to decrease. This means that as L is reduced the current density will be higher for a given current because this current can be achieved in a shorter period of time. As a consequence of this shorter time period required to attain the given current, the diameter of the spark channel is smaller because it has less time to expand (68,121). Increases in the breakdown potential also result in a more energetic spark discharge.

The capacitance (C) has a smaller influence on the character of the discharge. As C is increased the period is lengthened and the peak current is increased. Although these two effects influence the current density in opposite directions, there is a small increase in current density (68,121).

High-voltage sparks have been characterized in detail from the time of the breakdown of the gaps to the period of afterglow (8,21,23,52,68,102,106,118). Time-resolved studies with rotating mirror techniques have enabled the different stages of a spark to be analyzed.

Although most of the current in high-frequency spark discharges is carried by electrons, the bombardment of the cathode with positive ions (sputtering) is the predominating mechanism of sample transport into the analytical gap (3,52, 106). The initial gap breakdown in each spark train forms an abundant supply of sputtering ions which are representative of the ionized constituents of the supporting atmosphere. Since there is little or no sample vapor in the analytical gap at the start of each spark train, the initial gap breakdown in each train makes no contribution to the excitation of the sample spectrum.

The sputtered electrode material, in the form of vapor clouds, is ejected from the cathode with velocities of 10^2 to 10^3 m/sec. The direction of the sample vapor cloud deviates from the direction of the spark streamer; the vapor cloud does not carry current for that discharge. However, the vapor cloud must expand into the path of the spark streamer since emission lines of the sample are observed during the latter portion of the first half-cycle of the spark discharge. For example, Bardocz (8) has obtained time-resolved spectra illustrating that at first only radiation representative of the spark breakdown was emitted. Succeeding spectra were caused by emission from the ionized constituents of the atmosphere (nitrogen and oxygen). Finally the spectrum of the electrode material was observed at the end of the first half-cycle of the spark discharge. This illustrates that the sample vapor is generated and excited during the same half-cycle of the discharge.

The principal excitation processes occurring in a spark discharge involve single or multiple collisions between sufficiently energetic electrons and atoms of the sample vapor (23,51,106). Excitation or ionization of a sample atom by a single electronic collision may be followed immediately by the bombardment of the excited atom or ion with other energetic electrons. Consequently, the atom or ion may be excited to still higher energy levels. From kinetic theory considerations and experimentally determined values of total collision cross-sections (73), the total number of collisions possible between N electrons and one sample atom can be approximated. The measured collision cross-sections vary considerably from element to element and also with electron energy. For a mean energy of 2.6 eV, corresponding to a temperature of 20,000°K, the total collisional cross-sections vary from 2.3×10^{-16} cm^2 for neon to 310×10^{-16} cm^2 for cesium (73). Assuming a current density for the spark of 10^5 A/cm^2, the total number of collisions, elastic and inelastic, occurring during the lifetime of an excited atom (10^{-8} sec) are estimated to be about 1 for neon, 3 for helium, 9 for thallium, 10 for argon, 16 for krypton, 27 for xenon, 31 for mercury, 34 for zinc, 41 for cadmium, 94 for sodium, 143 for potassium, and 193 collisions for cesium. Thus even if only 50% of these collisions are inelastic, additional excitation or ionization resulting from multiple collisions of electrons with sample atoms or ions is quite probable for most of the above elements. The number of electronic collisions is related to the electron density of the source and consequently increases in discharges of high current density. Thus the high current densities of a spark, about 10^5 to 10^6 A/cm^2 compared to 10^2 A/cm^2 for an arc, account for the spectra of ions and high-energy lines that are obtained with a spark discharge (68).

The nature of the excited sample spectrum varies with time during a single discharge. Time-resolved studies of the emitted radiation from a spark have shown that during the initial current pulse the intensities of the ion lines are high compared to the intensities of the neutral atom lines. At this time the temperature in the core of the spark may be as high as 40,000°K (8,68) and under these conditions high ionization is expected. With succeeding current oscillations, the current decreases and the temperature drops rapidly. With a lower temperature there is less ionization, the intensity of the ion lines decreases, and the atom lines exhibit an increase in intensity. Near the end of the discharge train the temperature is sufficiently low so that the neutral atom lines become weak and finally disappear.

The use of a source, such as the spark discharge, characterized by high temperatures and high ionization should be conducive to the excitation of the high-energy halogen ion lines. The intensity of the neutral atom lines, however, would be expected to decrease because of the large amount of ionization in the spark.

V. APPARATUS AND PROCEDURE

A. Excitation Chamber

A controlled atmosphere chamber (Spex Industries, Inc. Model No. 9700) was extensively modified for this research. Of the original lower electrode stage assembly, only the baseplate (hereafter referred to as the lower electrode stage), gear set, and rotary shaft were kept. These last two items served to rotate the lower electrode stage. A total of 11 collets, 15.7 mm long, could be accommodated in the lower electrode stage but only 5 collets were normally loaded at one time. These collets (E in Figure 4), made from phosphor bronze, were designed to tightly hold the sample pellets and to fit snugly into the lower electrode stage, thereby ensuring good electrical contact. The entire lower stage was grounded, hence all five collets and their accompanying sample pellets assumed the same potential during excitation.

The upper, rotating electrode stage was designed to accommodate five collets (D in Figure 4), 18.8 mm in length, which in turn held the sample pellets. The electrical power was applied to the upper electrode stage. Thus, all the electrodes in the upper stage assumed the same potential. To prevent simultaneous sparking between the upper and lower pairs of electrodes in the two stages, the upper electrode stage (C) was inclined at 45^{o} from the horizontal as shown

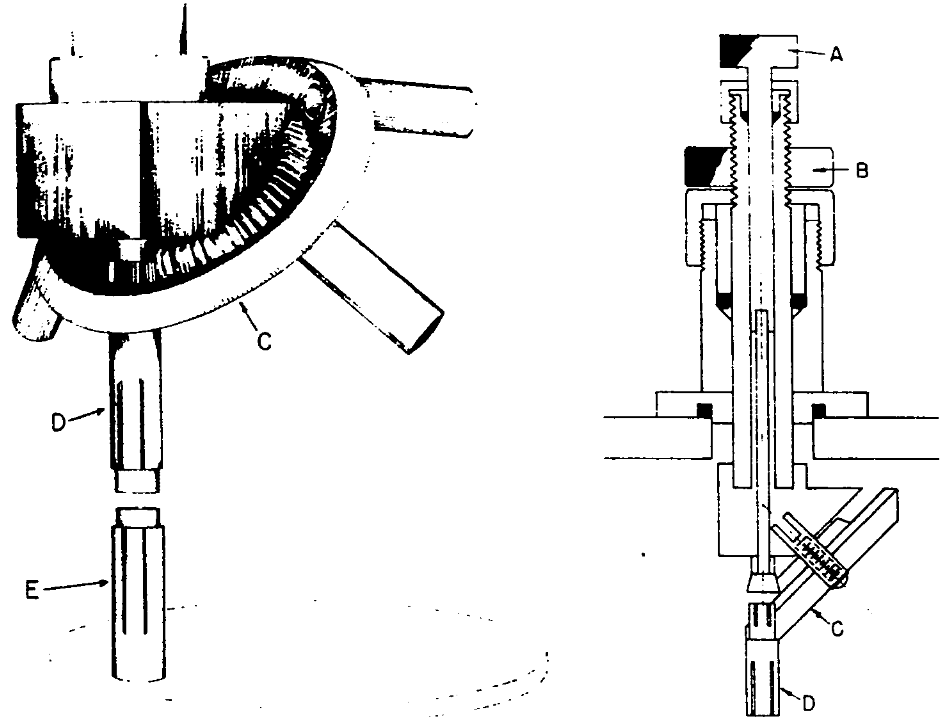


Figure 4. Upper electrode stage assembly: left-alignment; and right-design of upper electrode stage

in Figure 4. Rotation of the upper stage (by means of knob A) then made it possible to bring a pair of electrodes into vertical alignment while all other electrode pairs exceeded the critical spark breakdown distance. The analytical gap separation was adjusted by raising or lowering the entire upper electrode stage with nut B.

With the previously indicated collet lengths, a simple inversion of the Pyrex glass separator brought the side-arm, with a quartz optical window, on axis with the analytical gap. The design of the lower electrode stage allowed the use of glass shields (shown in Figure 5) behind each pair of electrodes. The shields eliminated or considerably reduced the possibility of cross-contamination. These shields consisted of 1/3 sections of a cylinder cut 38 mm long from 42 mm diameter Pyrex tubing.

Figure 5 illustrates the alignment of the electrodes in the upper and lower electrode stages. The arrangement of the electrodes, glass shields, and Pyrex cylinder in the excitation chamber is also shown. Marinite 36 insulation was placed around the upper platform to prevent electrical shocks.

B. Vacuum System

The vacuum and gas-handling system is illustrated in Figure 6. Cylinders of helium (B) and argon (C) provided the gas for the chamber atmosphere. The pressure of the gas in

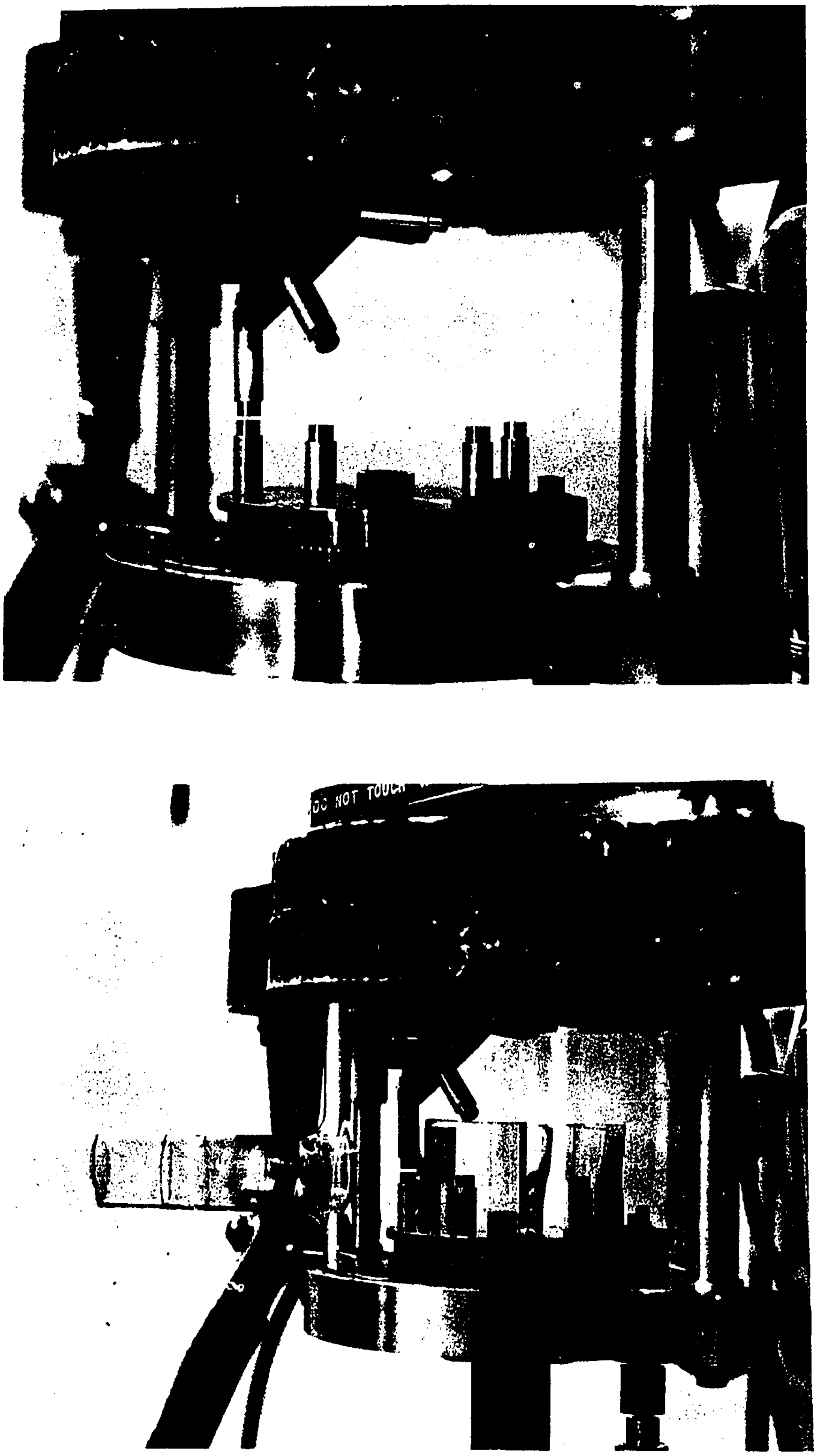
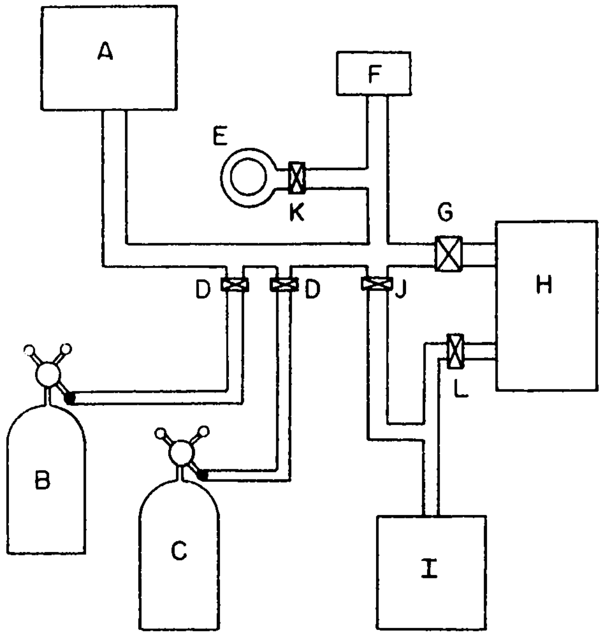


Figure 5. Photographs of excitation chamber



A	EXCITATION CHAMBER
B	HELIUM TANK
C	ARGON TANK
D,J,K	HOKE TOGGLE VALVES, SERIES 450
E	WALLACE & TIERNAN PRECISION ANEROID MANOMETER; NO. FA-129
F	PHILIPS GAUGE; CVC NO. PHG-01
G	HILLS-McCANNA 1-INCH BALL VALVE
H	NRC AIR-COOLED, OIL DIFFUSION PUMP; MODEL HSA-150
I	WELCH VACUUM PUMP; NO. 1402B
L	JAMESBURY 1-INCH BALL VALVE

Figure 6. Vacuum system

the excitation chamber was measured with a pressure gauge (E) (Wallace and Tiernan, No. FA-129). Low pressures were measured by a Philips gauge (F). Ball valves (G) and (L) isolated the diffusion pump (H) during the initial evacuation of the excitation chamber by the mechanical pump (I).

C. Spectrographic Facilities

A description of the Jarrell-Ash, 3.4 meter, Ebert spectrograph and photographic processes that were used may be found in Table 3. The external optical system, designed to provide uniform illumination over the entire length of the spectrograph slit, was similar to the three-lens system used by Feldman and Ellenburg (27). A spherical lens formed a 2:1 image of the electrodes on an intermediate diaphragm which had an aperture large enough to pass all of the light emitted within the analytical gap. A crossed cylindrical lens system positioned between the diaphragm and the slit of the spectrograph further modified the image so that the aperture of the spectrograph was completely filled. In order to align the electrodes prior to sample excitation, the electrode image was projected onto the diaphragm by the illumination of a light bulb located behind the excitation chamber.

Table 3. Spectrographic equipment and conditions

Spectrograph	
Type	Jarrell-Ash Company, 3.4 m Ebert mounting plane grating spectrograph
Grating	
Blaze	5000 Å in first order
Width	15.2 cm
Rulings	600 grooves/mm
Dispersion	5.1 Å/mm in first order
Wavelength coverage	2550 Å in first order
Slit width	0.05 mm
Development	4 minutes at 21°C in Eastman Kodak D-19 with continuous agitation
Microphotometer	National Spectrographic Laboratories, "Spec Recorder"
Emulsion calibration	Iron arc; two-step sector, preliminary curve method

D. Excitation Source

The high-voltage spark source on the National Spectrographic Laboratories (NSL) "Spec Power" unit was used for sample excitation. The electrical parameters available with the high voltage spark source were as follows: fixed inductance settings of 25, 50, 100, 200, 300, 600, and 1000 μh;

fixed capacitance settings of 0.0025, 0.0037, 0.0050, 0.0062, 0.0075, 0.0087, and 0.01 µf; and fixed resistance settings of 1, 2, and 3 ohms. A spark power setting which provides for an increase of power input into the spark transformer primary could be varied in ten equal steps. The voltage into the primary coil of the spark transformer could be varied by rotating the spark primary voltage Powerstat from one to 100 percent.

E. Sample Preparation

All sample mixtures were prepared by thoroughly mixing given amounts of sample and some matrix material utilizing an agate or boron carbide mortar and pestle. One part sample mixture was then thoroughly mixed with two parts of high purity, pelleting graphite (Union Carbide No. L4100).

Capped pellets, 6.4 mm in diameter, were prepared by placing approximately 0.06 g of the mixture of sample and graphite described above in a briquetting press (Applied Research Laboratories, No. 3502) and then adding approximately 0.5 g of pelleting graphite. The powder was pressed into pellets by a total load of 6000 pounds applied for 20 seconds. The resulting pellets were about 8 mm long.

F. Procedure

The pellets were mounted so that they extended approximately 4 mm above the collets. The electrode holders and glass shields were then loaded in the excitation chamber.

The chamber was evacuated with the mechanical pump and then flushed several times with the desired inert gas to reduce the original air content to a negligible amount. The chamber was then evacuated to a pressure of 4×10^{-4} Torr or lower as indicated by the Philips gauge, and refilled with the given gas to the desired pressure. After each sample excitation the chamber was evacuated with the mechanical pump, flushed, and recharged with the desired gas.

The chamber was tightened with C-clamps when the pressure of the gas in the chamber exceeded atmospheric pressure.

VI. OPTIMAL EXCITATION PARAMETERS FOR THE DETECTION OF THE HALOGENS

In theory and in practice, the detectability of the halogens and sulfur is influenced by many experimental variables. Some of the obvious variables are the following: electrode parameters, namely, analytical gap, electrode material and the use of two sample electrodes or a counterelectrode and a sample electrode; supporting atmosphere and pressure; and electrical parameters including capacitance (C), inductance (L), resistance (R), spark primary voltage (SPV), and spark power (SP). The primary criterion for the selection of the optimal experimental conditions is the highest line-to-background intensity ratios, I_L/I_{BG}, observed for the sensitive halogen lines as the experimental parameters were varied. The line-to-background intensity ratios reported later were calculated as follows:

$$\frac{I_L}{I_{BG}} = \frac{I_{(\text{LINE + BACKGROUND})}}{I_{\text{BACKGROUND}}} - 1$$

and represent the average of duplicate or triplicate runs. The sample used for all tests consisted of 0.6% fluorine, 0.25% chlorine, bromine, iodine, and sulfur respectively in a stannic oxide matrix.

A. Considerations of Electrode Phenomena

1. Supporting electrode material

One of the requirements for a qualitative analysis scheme of general applicability is that the vaporization and excitation technique should be directly applicable to all types of solid samples, conducting or non-conducting. However, for high-voltage spark excitation, the supporting electrodes must be good conductors. One of the generally successful approaches to this problem is to incorporate the non-conducting sample into a conducting electrode material and form conducting pellets from these blends. In the past, powdered graphite, copper, and silver have been used as supporting conductors.

Tables 4 and 5 show typical line-to-background intensity ratios observed during evaluative experiments of copper, silver, or graphite as the conducting electrode material. The data for these tables were obtained with the following parameters: 0.0037 μf, SP 10, SPV 70, two sample electrodes, 1.5 mm analytical gap, and a helium supporting atmosphere at a pressure of 400 Torr for Table 4 and 760 Torr for Table 5. Unless indicated otherwise, only the residual inductance and resistance inherent to the source unit were used. Other combinations of electrical parameters gave no noticeable deviation from the relative results summarized in these tables. Thus it is clear that graphite electrode material possessed a definite superiority in providing larger I_L/I_{BG}. However, the I_L/I_{BG} of the chlorine lines were consistently as good or better for silver than for graphite. No explanation for this deviation can be offered. However, the absence of chlorine contamination was demonstrated from the spectrum of a silver pellet. The behavior of copper and silver powders during the pellet forming process was also inferior to graphite. There was a tendency for galling to occur between the metallic pellets and the die during the pelleting process. Eventually this resulted in the die becoming inoperative. Also, during the sparking process, part of the top of the copper pellets usually broke off, causing large fluctuations in the I_L/I_{BG}.

Table 4. Comparison of graphite and silver

Line (Å)	$I_{Line}/I_{Background}$	
	Graphite	Silver
Cl II 4794.54	3.4	3.6
I II 5161.19	3.0	1.0
S II 4162.70	1.5	0.97
F II 3505.61	0.33	not measurable

Table 5. Comparison of graphite and copper

Line (Å)	$I_{Line}/I_{Background}$ Graphite	Copper
Br II 4785.50	2.6	0.75
Cl II 4810.06	2.1	0.32
Cl II 4819.46	1.4	0.39
S II 5453.81	1.0	0.72
I II 5464.62	0.92	0.32

The direct excitation of metal self-electrodes in a helium supporting atmosphere presented some unexpected problems. For example, with steel electrodes, the discharge engulfed the electrodes about one second after the sparking started and subsequently spread to the collets. Very little sampling of the top surfaces of the steel electrodes occurred. No significant improvement in this objectionable behavior was evident as the pressure and supporting atmosphere (about 400 to 760 Torr helium, argon, helium and air mixture, and argon and air mixture) were varied. Kaiser and Wallraff (53) observed similar phenomena with iron, copper, platinum, and silver. This difficulty was corrected by incorporating filings prepared from massive samples into graphite supporting briquettes which could then be sparked successfully.

2. Two sample pellets or a counterelectrode and a sample pellet

In high-voltage spark excitation, the individual sparks are passed either between a counterelectrode and the sample or between two sample electrodes. Because cathodic sputtering of samples occurs during both half cycles, it is expected that greater I_L/I_{BG} would be observed when both electrodes were composed of the sample mixture. The improvement in I_L/I_{BG} achieved with the above arrangement became apparent early in this study. A typical set of results is given in Table 6. All subsequent experiments were performed with two sample electrodes.

Table 6. Use of sample electrode and counterelectrode or two sample electrodes

Line (Å)	$(I_{Line}/I_{Background})^a$ Two sample electrodes	$(I_{Line}/I_{Background})^a$ Counterelectrode and sample electrode
Br II 4704.86	2.3	.84
Br II 4785.50	1.8	.65
Cl II 4794.54	3.0	1.2
Cl II 4819.46	1.0	.56
I II 5161.19	1.1	.54
S II 5453.81	.78	.48

[a] Experimental conditions: 0.0037 μf, SP 10, SPV 70, 1.5 mm analytical gap, helium at 690 Torr.

3. Analytical gap

The line to background behavior of several lines of the halogens and sulfur as a function of gap separation is illustrated in Figure 7. The improvement in I_L / I_{BG} with decreasing analytical gap separation was expected and this confirmed the earlier observations of Fizalkowski *et al*. (28,29). Since the breakdown voltage of the analytical gap remains constant as the analytical gap width is decreased, it follows that the energy dissipated ($\frac{1}{2}CV^2$) per spark train will remain the same. Thus, both the energy and the sample vapor concentration per unit volume are expected to increase with decreasing gap separation. Consequently, the sample vapor should be more efficiently excited in smaller gaps. However, analytical gaps smaller than 1.5 mm showed a surprising drop in overall spectral intensity. Part of this intensity decrease can be attributed to vignetting or shadowing of the emitted radiation by the electrodes. However, this purely geometrical consideration cannot totally account for the observed spectral changes. In addition to the overall intensity decrease, the more energetic lines, for instance the lines of Sn II, He I, and the ion lines of the halogens, were depressed to a greater extent than lines originating from lower excited states.

Branching of spark streamers (65) has been known to occur under condition of high overvoltage (voltage in excess of the amount required to break down the gap). Thus, branch-

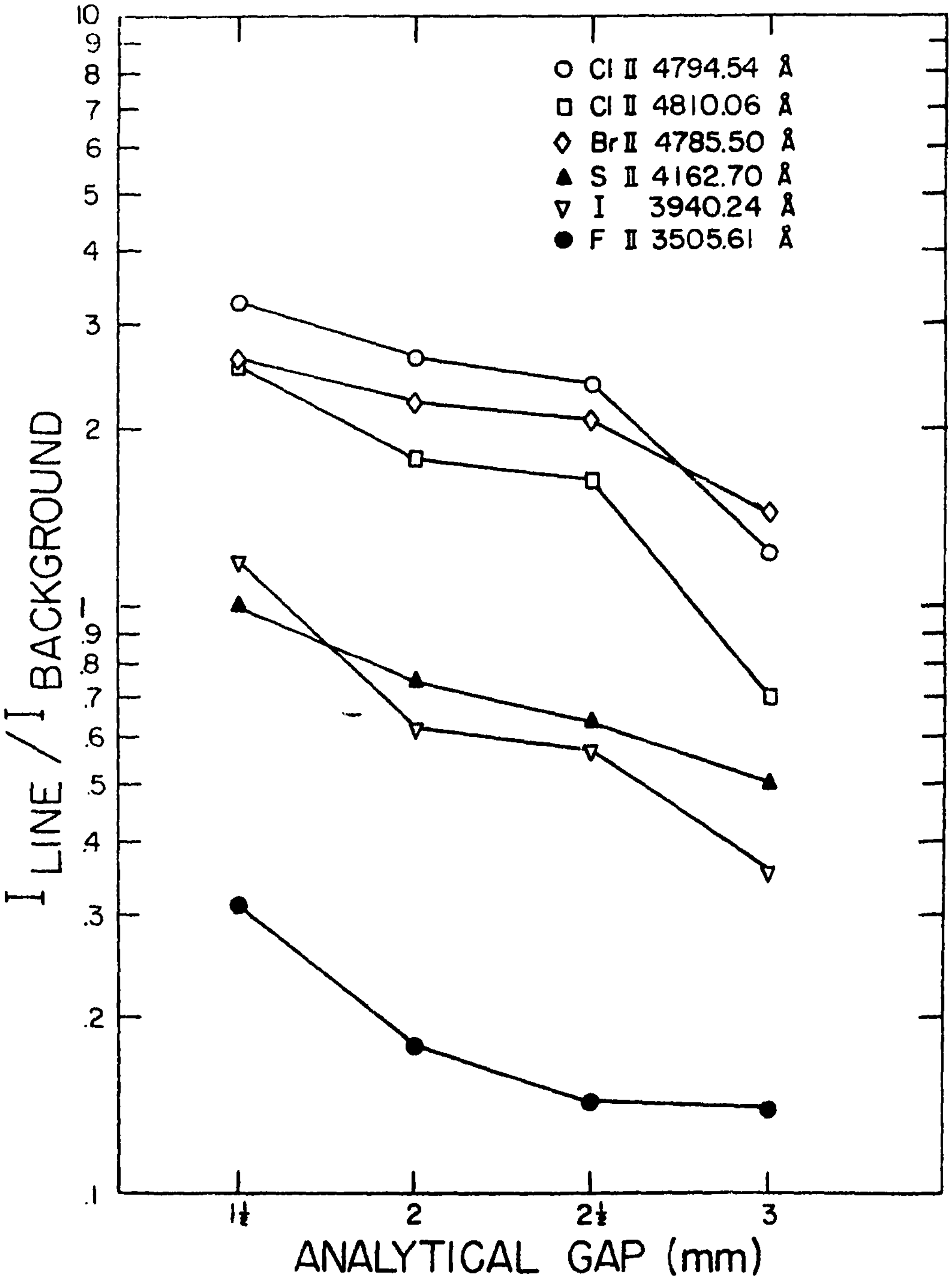


Figure 7. Effect of analytical gap width on I_L/I_{BG} under the following conditions: helium at 400 Torr, 0.0037 μf, 25 μh, SP 10, SPV 70

ing should occur to a greater extent for small gaps. One of the consequences of such branching should be a decrease in the current density of the individual branches when compared to the current density of the usual single streamer per breakdown. Because high current densities are important in populating the excited states of the halogens and sulfur (see chapter IV), branching of spark streamers may account for the experimental observations. The plausibility of this hypothesis was explored in the following manner: highly-polished, silver pellets were sparked for 4 seconds across 1 and 2 mm gap separations. A far greater number of sputtering pits, indicating a correspondingly greater number of streamers, were observed in the pellets sparked across a 1 mm gap separation than in the pellets sparked across a 2 mm gap separation.

B. Nature and Pressure of the Supporting Atmosphere

The composite sample vaporization and excitation mechanism is influenced by the nature and pressure of the supporting atmosphere, as seen from the discussion presented in Section III-B-2. In review, the vaporization efficiency is expected to be greater as the number of ions of the supporting atmosphere increase (at increasing pressures) and as the energy acquired by the ions increases (at decreasing pressures). Also, at low pressures the electrons possess higher energies and have a greater probability of populating high-energy excited states.

With reference to the selection of a noble gas supporting atmosphere, argon ions should be better sputtering ions than helium because of their greater mass. However, an earlier discussion (Section III-B-1) of energy distributions in argon or helium spark plasmas indicated that the latter should be a more desirable supporting atmosphere.

Finally, a previous discussion (Section III-B-2) has demonstrated that the pressure and nature of the supporting atmosphere affect the continuous background emitted during the course of the spark discharge.

It is thus apparent that there are many possible permutations of the nature and pressure of the supporting atmosphere. In order to reduce the number of these experiments to a manageable magnitude, neon, krypton, and xenon were not studied because they were considered too expensive for practical qualitative analyses.

In the discussion that follows, some of the most significant observations made during these experiments are summarized.

1. Pressure variation in a helium atmosphere

The effect of pressure variation in a helium atmosphere on I_L/I_{BG} is shown in Figure 8. It is seen that the I_L/I_{BG} are relatively constant between 260 and 760 Torr. The slight decrease in I_L/I_{BG} above 760 Torr was the consequence of an increase in the background level, as shown in Figure 9. This

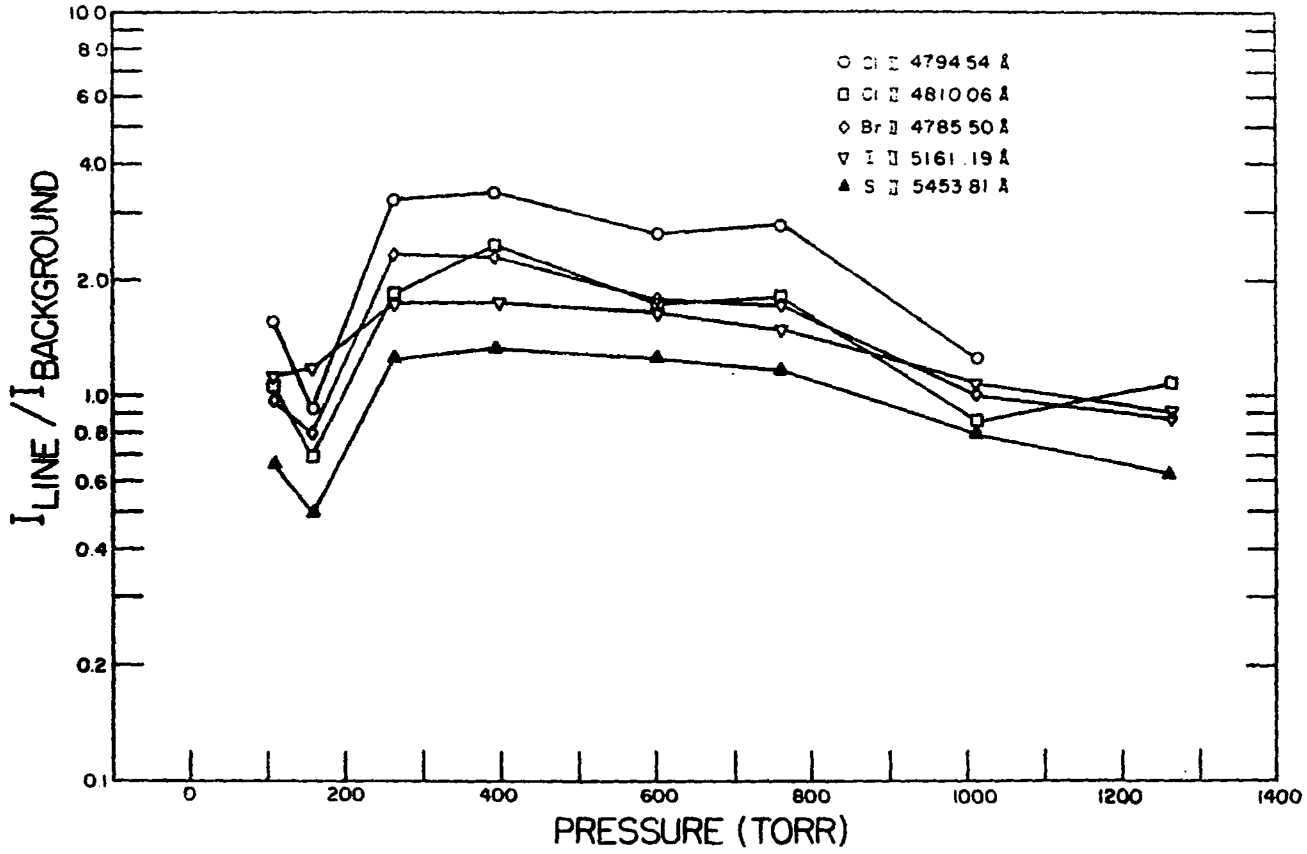


Figure 8. Pressure study in helium under experimental conditions of: 0.0037 μf, SP 10, and SPV 70

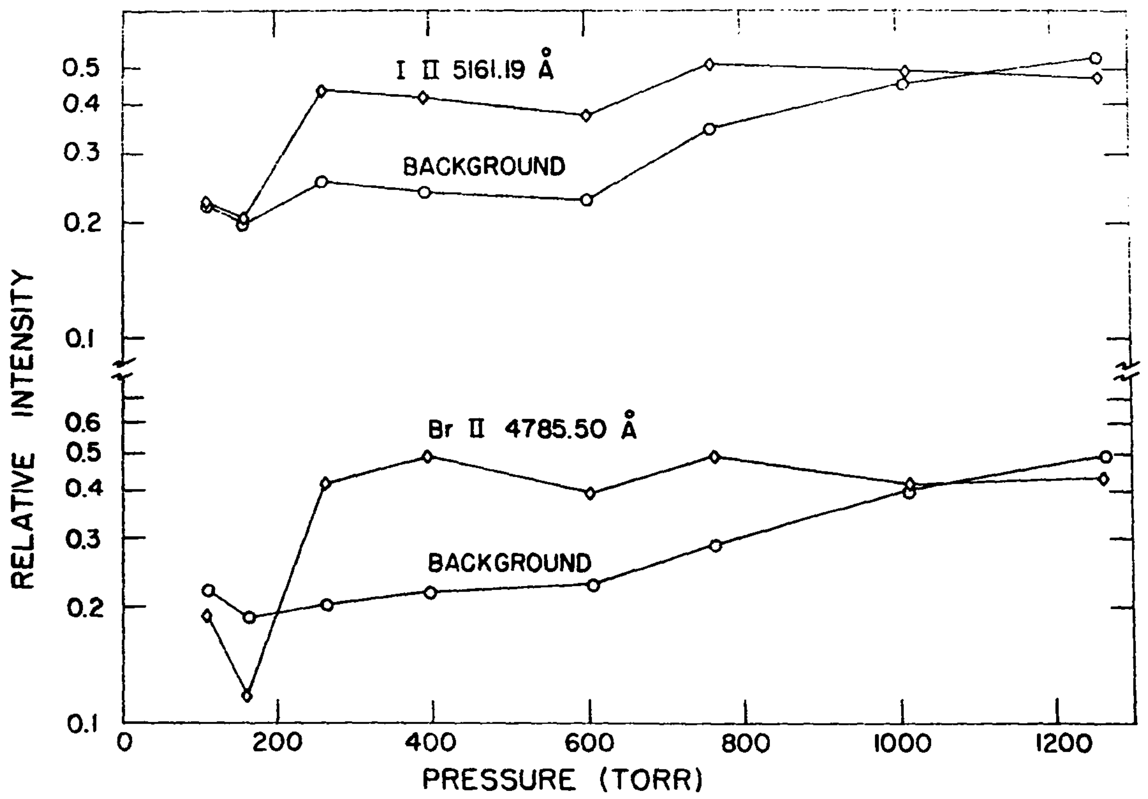


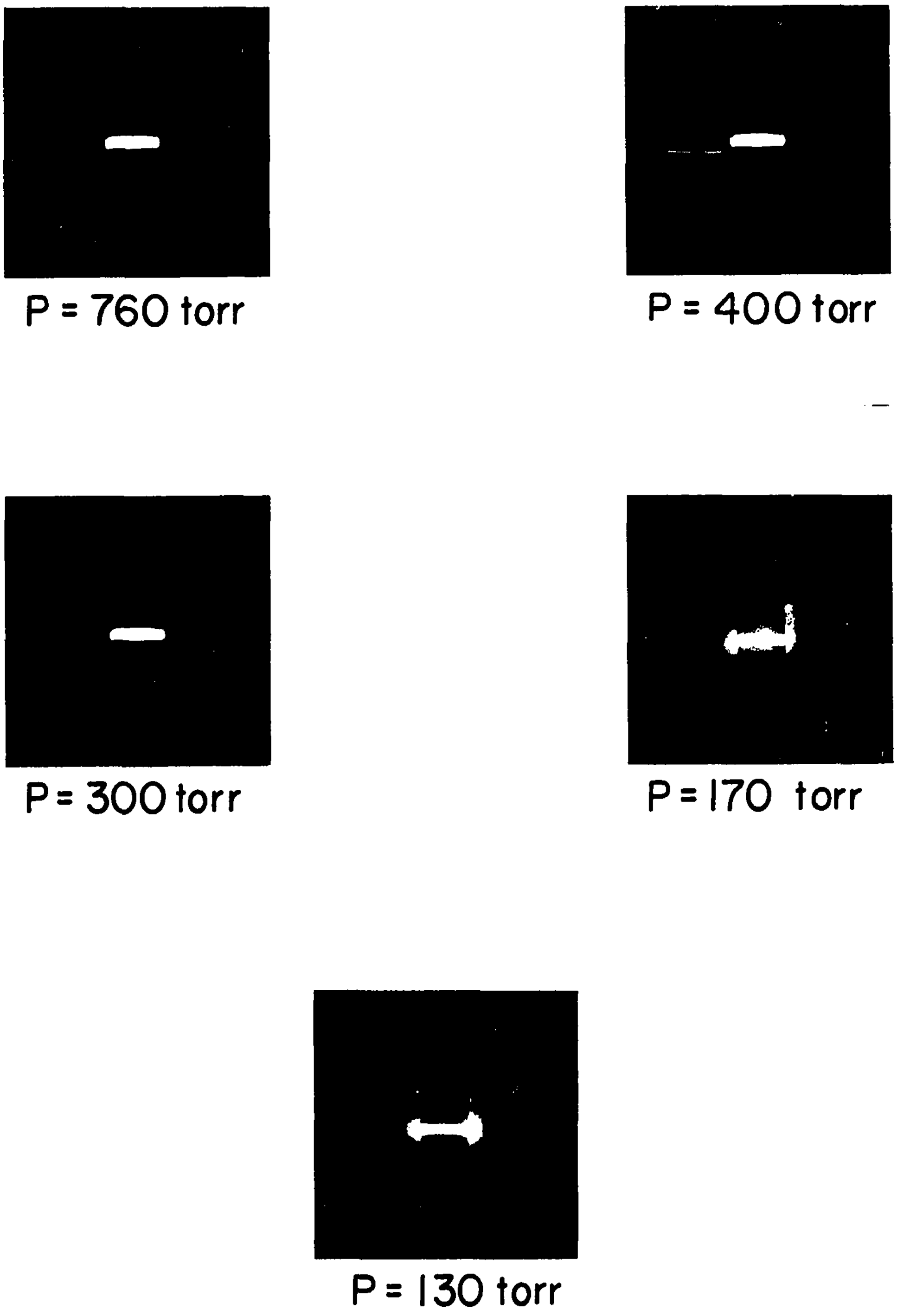
Figure 9. Change in relative line and relative background intensity with pressure in helium using electrical parameters of: 0.0037 μf, SP 10, SPV 70

increased background was not unexpected because with increasing pressure there are more ions available to participate in processes (Section III-B-2) that result in the emission of background radiation.

As the pressure was decreased below 260 Torr, the spark exhibited an increasing tendency to engulf the pellets and collets. This behavior is illustrated in Figure 10. It is apparent that at pressures of 130 and 170 Torr, portions of the spark discharge are, in fact, striking the collets. Thus at pressures below 260 Torr this excitation process was not considered practical.

From the foregoing discussion, it is apparent that pressures in the range of 260 to 760 Torr not only provided the maximal I_L/I_{BG} but also produced well behaved spark discharges. Because the pressure of 400 Torr showed a slight but definite superiority not only in I_L/I_{BG} but also in the absolute level of the background, this operating pressure was selected for further study.

The effect of changing excitation parameters on the I_L/I_{BG} of the halogens at the constant pressure of 400 Torr in helium is illustrated in Figure 11. It is seen that maximal I_L/I_{BG} are obtained when both resistance and inductance are at residual or low settings. This is expected if it is remembered that as the values of R and L decrease, a higher peak current and a more energetic spark are obtained (Chapter



P = 760 torr

P = 400 torr

P = 300 torr

P = 170 torr

P = 130 torr

Figure 10. Spark discharge at different pressures

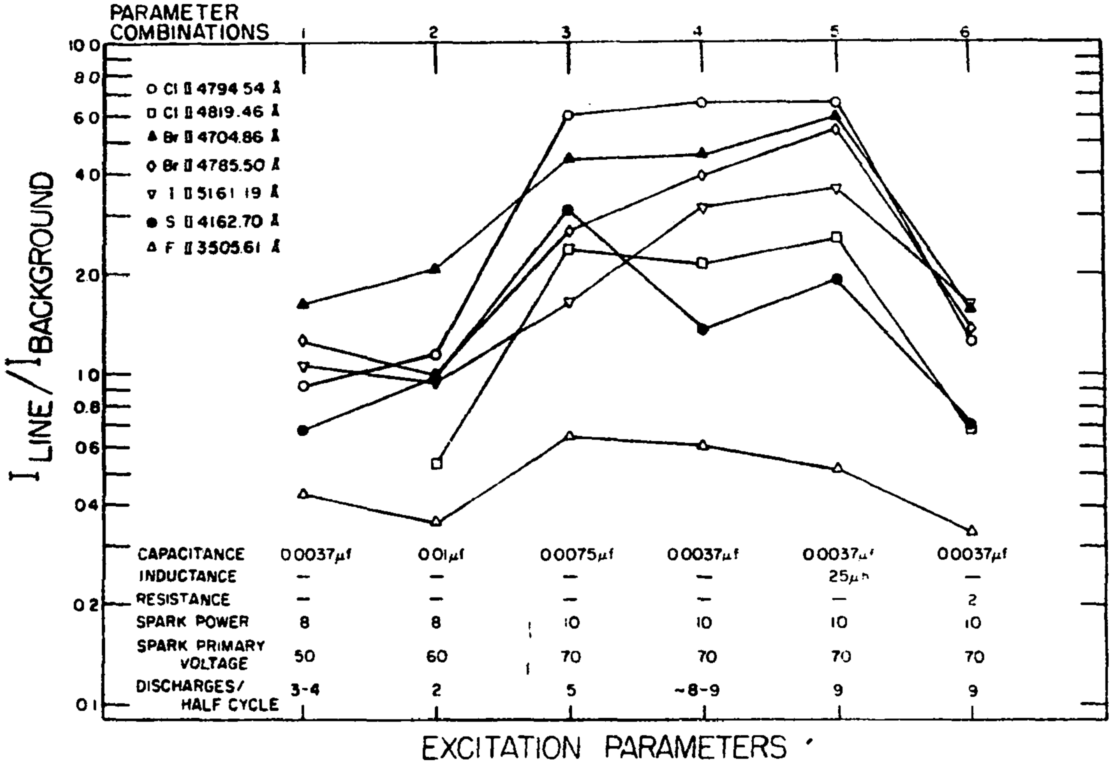


Figure 11. Effect of various electrical parameters

IV).

A decrease in capacitance, as seen in runs 3 and 4 at constant primary voltage, had little effect on the I_L/I_{BG}. This is in concurrence with the idea that a change in C has a correspondingly small effect on the resulting current density. Also, because an increase in C results in an increase in the time required for the condensers to charge to a given voltage level, fewer discharges per half-cycle were expected. This, in fact, was observed as indicated in runs 3 and 4 of Figure 11.

A maximum amount of spark power (SP 10) and a high value of spark primary voltage are important for high I_L/I_{BG} (see runs 1 and 2 in Figure 11). An increase in the SP and SPV causes the condensers to be charged at a faster rate which results in more discharges per half-cycle and consequently more sampling of the electrodes. Although a minimum SPV of 70 was necessary (Figure 12), a further increase in the SPV did not substantially change the I_L/I_{BG} until they decreased slightly at the maximum SPV. A disadvantage of employing maximum spark primary voltage was that the audio noise level of the spark became increasingly annoying to the operator and his fellow workers.

The electrical parameters 0.0037 μf, 25 μh, SP 10, and SPV 70 were selected as optimal. However, it is apparent from Figure 11 that parameter combinations 3, 4, and 5 also pro-

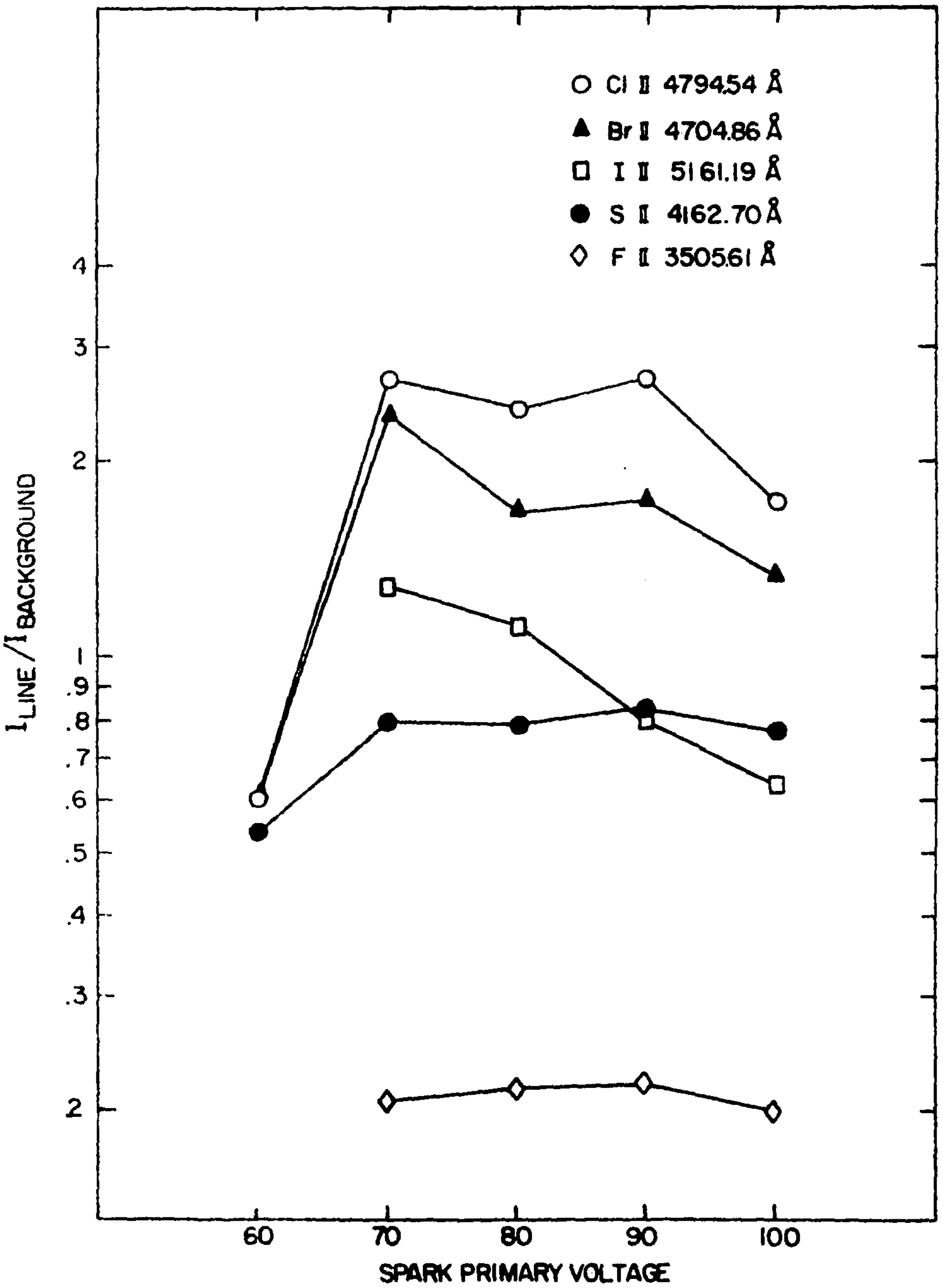


Figure 12. Variation of spark primary voltage using excitation conditions of: helium at 400 Torr, 0.0037 μf, 25 μh, and SP 10

vided maximal I_L/I_{BG}, and thus any of these combinations would be a logical selection. However, this excitation technique must also provide good powers of detection for all the other elements. Because most metallic elements have low-lying excited states, it is therefore desirable to select the combination that corresponds to the less energetic spark. Thus, of the three preceding possibilities the one with the added inductance and least capacitance was selected.

2. Pressure variation in an argon atmosphere

Figure 13 illustrates that for an argon atmosphere the I_L/I_{BG} of the halogen lines reached a maximal value at a pressure of 75 Torr and then decreased with a further increase in pressure. This was expected because in an argon atmosphere, the probability for the effective excitation of the halogen lines would be greatest at low pressures (Section III-B-2). As illustrated in Figure 14, the background radiation increased rapidly with increasing pressure and was so intense at pressures of 400 Torr and greater that difficulty was encountered in measuring I_L/I_{BG}. It was obvious that the background radiation was more intense and became significant at lower pressures in argon compared to helium. Several other investigators have reported heavy background emission in arc discharges in argon atmospheres (72,112). These observations are consistent with theoretical predictions. The efficiency of ionization by electrons is much higher and occurs at much

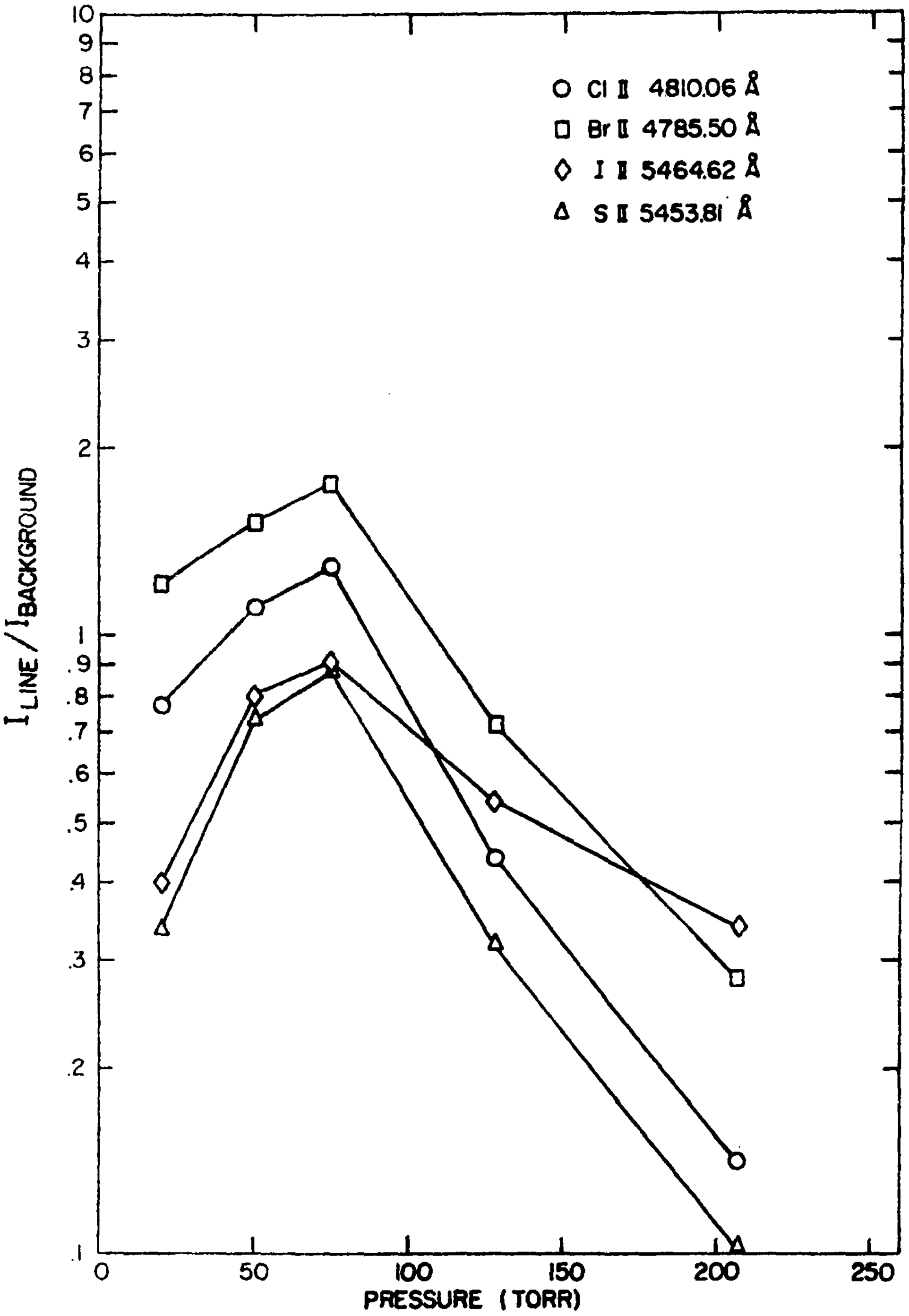


Figure 13. Pressure study in argon using electrical parameters of: 0.0075 μf, 50 μh, SP 10, and SPV 70

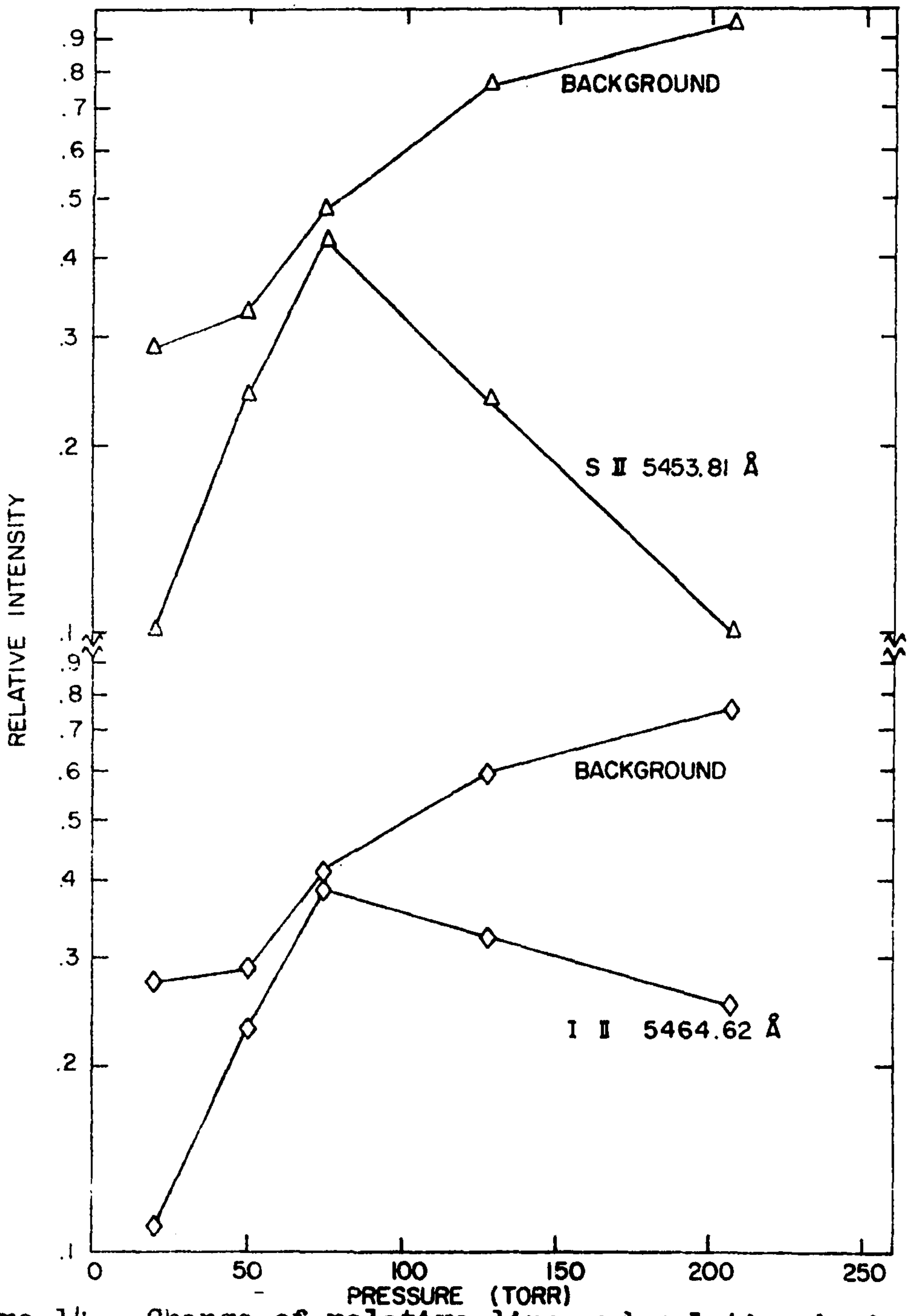


Figure 14. Change of relative line and relative background intensity with pressure in argon using electrical parameters of 0.0075 µf, 50 µh, SP 10, and SPV 70

lower energies in argon than in helium (66) and therefore, the absolute number of ions and consequently, the amount of background radiation should be greater for an argon atmosphere. Also the intensity of background radiation due to free-free transitions and recombination processes is greater for heavier elements (34).

The results of experiments similar to those performed for helium (and illustrated in Figure 11) showed that at 75 Torr in argon, capacitances in the range 0.005 to 0.01 μf, residual resistance, 50 μh, SP 10, and SPV 70 provided maximal I_L/I_{BG} for the sensitive halogen lines. However, the F I 6856 Å line was either very faint or not detectable at the 0.6% concentration level. This fact in itself renders an argon atmosphere not acceptable for this purpose.

3. Comparison of I_L/I_{BG} ratios in helium and argon at selected optimal pressures-electrical parameters

The high energy lines of the halogens were more effectively excited in helium than in argon as demonstrated by the data summarized in Table 7. The most sensitive fluorine atom line was, in fact, not detectable in the argon atmosphere. This is really not too surprising because 14.4 eV are required to excite this line. Because the lowest excited state in argon is at 11 eV and the ionization potential is 15.8 eV, the relative number of electrons with sufficient energy to excite the fluorine line should be far less than for the helium atmosphere. For the latter atmosphere, the lowest excited state and the ionization potential are at 19.8 and 24.6 eV.

Table 7. Comparison of helium and argon atmospheres

Line (Å)	$I_{Line}/I_{Background}$	
	He[a] at 400 Torr	Ar[b] at 75 Torr
Br II 4704.86	6.1	3.1
Br II 4785.50	4.3	1.8
Cl II 4794.54	6.1	3.0
I II 5161.19	1.7	1.2
S II 5453.81	1.5	0.97
F I 6856.02	1.3	not seen

[a] Electrical settings: 0.0037 μf, 25 μh, SP 10, SPV 70.

[b] Electrical settings: 0.005 μf, 50 μh, SP 10, SPV 70.

C. Effect of Various Matrix Materials

In all the experiments described previously, stannic oxide was used as a supporting matrix for the halogens and sulfur impurities in the sample pellet. It is appropriate to note why this matrix was chosen. Such a matrix should have a simple emission spectrum, be nonhygroscopic, and be easily obtained in a fairly pure form. Stannic oxide satisfies these requirements but any other material meeting these criteria should be just as satisfactory.

During the performance of experiments designed to aid in the selection of an appropriate matrix, several important observations were made which had a bearing on this selection as well as on the ultimate practical application of this excitation technique.

The physical behavior of the discharge varied when different matrix materials, mixed with graphite, were sparked in helium at 400 Torr with instrument parameters of 0.0037 µf, 25 µh, SP 10, and SPV 70. Zinc oxide, stannic oxide, lead dioxide, and cadmium oxide were among the several oxide matrices which gave excellent sparking behavior.

However, during the excitation of blends of the alkaline earth oxides or thorium dioxide with graphite, the spark discharge exhibited an objectionable tendency of occasionally striking the sides of the pellets. In the case of thorium dioxide, the discharge completely engulfed the pellets and even part of the collets. The cause of this spreading discharge is not known, but it might be explained in part by the thermal emission of electrons from these materials. It is well known that the alkaline earth oxides are used to coat the cathodes in electron tubes when high electron emission at low temperatures is desired. It is therefore possible that when the sample becomes warm, electron emission may occur. This would account for the expansion of the discharge. This behavior is a serious limitation to the practical utilization of these excitation conditions because the spectrum of collet materials may also be recorded. In an effort to find a possible solution to this problem the matrix material was diluted to a greater extent with graphite. However, increased dilution of barium oxide or thorium dioxide, from 1:2 to 1:10 with graphite increased the amount of spark wander. This behavior with a higher proportion of graphite in the pellets was not surprising. The spark discharge tends to wander when pure graphite pellets are used (discussed in Section VII-A). Thus as barium oxide and thorium dioxide were diluted, the pellet became more like a pure graphite pellet and consequently there was still spark wander. However, for blends of barium oxide and graphite all stray sparking was eliminated by increasing the pressure to 760 Torr. Also, at this pressure, the discharge no longer engulfed pellets containing a 1:2 blend of thorium dioxide and graphite. However after about one minute, the discharge occasionally sparked to the sides of these pellets.

Excitation at 760 Torr should have little effect on the powers of detection for the halogens because pressures of 260 to 760 Torr in helium yielded approximately equivalent I_L/I_{BG} (Section VI-B-1). A pressure of 400 Torr had been originally selected because the I_L/I_{BG} were somewhat higher and the level of background was less.

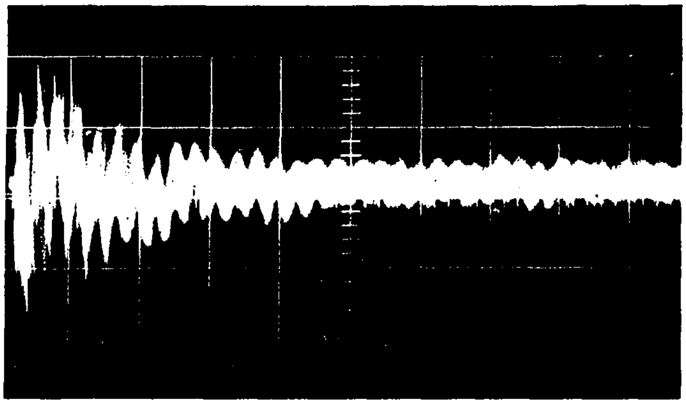
D. Summary of the Optimal Excitation Variables for the Detection of the Halogens

In several instances equivalent I_L/I_{BG} for the sensitive halogen lines were obtained for different combinations of excitation parameters. The variables that were chosen as the optimal experimental conditions for the detection of the halogen lines are summarized in Table 8. The reasons for each selection have been presented in prior sections.

Oscilloscope tracings illustrating a single spark train and also the number of such spark trains obtained in a given half-cycle, for these spark parameters, are seen in Figure 15.

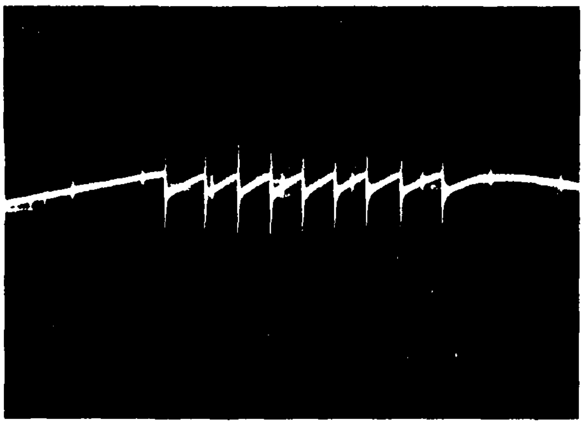
Table 8. Optimal experimental conditions

Source unit	National Spectrographic Laboratories, "Spec Power" Model KE-4144
Source	High voltage spark
Capacitance	0.0037 µf
Inductance	25 µh
Spark power	10
Spark primary voltage	70
RF current (rms)	~13 amps
Voltage (rms)	~20,500 volts
Electrode system	2 sample pellets with flat tops, 6.4 mm diameter
Electrode material	High purity, pelleting graphite powder
Analytical gap	1.5 mm
Atmosphere	400 Torr He



a

10 μsec/cm



b

5 msec/cm

Figure 15. Oscilloscopic tracings of the current waveform: (a) for a single spark train; and (b) illustrating the number of spark trains in a given half-cycle

VII. DETERMINATION OF THE SENSITIVE LINES AND A QUALITATIVE DETECTION LIMIT FOR MOST ELEMENTS

Prior to the establishment of a practical qualitative analysis scheme using the previously determined excitation conditions, it was necessary to select the sensitive lines and determine the limits of detection of all the elements included in such a scheme. Only the synthetic and radioactive elements and noble gases were omitted from this study.

Because of the nature of the excitation, more sample ionization is expected and consequently in many instances, the ion lines will be more sensitive than the atom lines of the analyte elements.

A. Sample Preparation and Procedure

Using the previously determined excitation conditions (Table 8), identification spectra for each element were prepared for the 2200-8800 Å spectral region. The analyzed samples consisted of approximately one percent by weight of each element respectively, in graphite pellets. The photographic plates and filters used in the different wavelength regions are listed in Table 9. The more intense lines for each element were identified by utilization of the reciprocal linear dispersion of the Ebert Spectrograph and various wavelength tables (37,76,122).

Table 9. Photographic emulsions and filters

Wavelength region (Å)	Photographic emulsion	Filter
2200-4700	Eastman III-0	None
4500-7000	Eastman II-F	Corning 0-52
6600-8900	Eastman I-N	Corning 2-63

As the concentration of an element in a discharge column is decreased, the number of observable lines is reduced until finally only the most sensitive lines, or raies ultimes, of the diluted element remain. In this manner the most sensitive lines of the various elements in a helium atmosphere were selected. In addition, a qualitative detection limit for these sensitive lines was determined in the following manner. A series of samples containing decreasing concentrations of an element in a given matrix, usually stannic dioxide, were prepared by diluting the original sample with stannic dioxide and then diluting each successive sample. Each of these samples was then mixed in a ratio of one part sample to two parts graphite. The simplest, purest compounds available for each element were used. When the number, location, and intensity of lines permitted, several elements were mixed together in a given series of samples. Table 10 gives the composition of the samples used for each element. Because of the impurities

Table 10. Composition of samples

Element analyzed	Sample[a]
Ag	AgCl, CuO, Fe_2O_3, and SiO_2 in ZnO
Al	Al_2O_3, Ga_2O_3, NH_4AuCl_4, and $(NH_4)_2PdCl_4$ in SnO_2
As	As_2O_3, Bi_2O_3, Se, and SiO_2 in SnO_2
Au	Al_2O_3, Ga_2O_3, NH_4AuCl_4, and $(NH_4)_2PdCl_4$ in SnO_2
B	CdO, H_3BO_3, $Hg(C_2H_3O_2)_2$, and ZnS in SnO_2
Ba	$BaCO_3$, BeO, $CaCO_3$, MgO, and $SrSO_4$ in SnO_2
Be	$BaCO_3$, BeO, $CaCO_3$, MgO, and $SrSO_4$ in SnO_2
Bi	As_2O_3, Bi_2O_3, Se, and SiO_2 in SnO_2
Br	NaBr, NaCl, NaF, $NaHSO_3$, and NaI in SnO_2
Ca	$BaCO_3$, BeO, $CaCO_3$, MgO, and $SrSO_4$ in SnO_2
Cd	CdO, H_3BO_3, $Hg(C_2H_3O_2)_2$, and ZnS in SnO_2
Ce	CeO_2 in SnO_2
Cl	NaBr, NaCl, NaF, $NaHSO_3$, and NaI in SnO_2
Co	Co_3O_4, $(NH_4)_2IrCl_6$, $(NH_4)_2OsCl_6$, $KReO_4$, and $(NH_4)_3RhCl_6 \cdot 1\frac{1}{2}\ H_2O$ in SnO_2
Cr	Cr_2O_3, MoO_3, Ta_2O_5, and WO_3 in SnO_2
Cs	Cs_2PtCl_6, KCl, Li_2CO_3, NaCl, and Rb_2PtCl_6 in SnO_2
Cu	AgCl, CuO, Fe_2O_3, SiO_2 in ZnO
Dy	Dy_2O_3 in SnO_2

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[a] Each of these samples was then mixed in a ratio of one part sample to two parts graphite.

Table 10. (Continued)

Element analyzed	Sample[a]
Er	Er_2O_3 in SnO_2
Eu	Eu_2O_3, Ho_2O_3, and Lu_2O_3 in SnO_2
F	NaBr, NaCl, NaF, $NaHSO_3$, and NaI in SnO_2
Fe	AgCl, CuO, Fe_2O_3, and SiO_2 in ZnO
Ga	Al_2O_3, Ga_2O_3, NH_4AuCl_4, and $(NH_4)_2PdCl_4$ in SnO_2
Gd	Gd_2O_3 in SnO_2
Ge	GeO_2, In_2O_3, Sb_2O_3, and TeO_2 in SnO_2
H	$NH_4H_2PO_4$ in SnO_2
Hf	HfO_2 and $Hg(C_2H_3O_2)_2$ in SnO_2
Hg	HfO_2 and $Hg(C_2H_3O_2)_2$ in SnO_2
Ho	Eu_2O_3, Ho_2O_3, and Lu_2O_3 in SnO_2
I	NaBr, NaCl, NaF, $NaHSO_3$, and NaI in SnO_2
In	AgCl, In_2O_3, PbO_2 in MgO
Ir	$[NH_4]_2IrCl_6$, $[NH_4]_2OsCl_6$, and $(NH_4)_2[Ru(H_2O)Cl_5]$ in SnO_2
K	Cs_2PtCl_6, KCl, Li_2CO_3, NaCl, and Rb_2PtCl_6 in SnO_2
La	LaF_3 in SnO_2
Li	Cs_2PtCl_6, KCl, Li_2CO_3, NaCl, and Rb_2PtCl_6 in SnO_2
Lu	Eu_2O_3, Ho_2O_3, and Lu_2O_3 in SnO_2
Mg	$BaCO_3$, BeO, $CaCO_3$, MgO, and $SrSO_4$ in SnO_2
Mn	CuO, Fe_2O_3, MnO_2, Ni, and Ru in SnO_2

Table 10. (Continued)

Element analyzed	Sample[a]
Mo	Cr_2O_3, MoO_3, Ta_2O_5, and WO_3 in SnO_2
N (as CN)	$NH_4H_2PO_4$ in SnO_2
Na	Cs_2PtCl_6, KCl, Li_2CO_3, NaCl, and Rb_2PtCl_6 in SnO_2
Nb	HfO_2, Nb_2O_5, TiO_2, and ZrO_2 in SnO_2
Nd	NdF_3 in SnO_2
Ni	CuO, Fe_2O_3, MnO_2, Ni, and Ru in SnO_2
O	SnO_2 in Ag
Os	$(NH_4)_2IrCl_6$, $(NH_4)_2OsCl_6$, and $(NH_4)_2[Ru(H_2O)Cl_5]$ in SnO_2
P	$NH_4H_2PO_4$ in SnO_2
Pb	CuO, Fe_2O_3, PbO_2, and SiO_2 in SnO_2
Pd	Al_2O_3, Ga_2O_3, NH_4AuCl_4, and $(NH_4)_2PdCl_4$ in SnO_2
Pr	Pr_6O_{11} in SnO_2
Pt	Cs_2PtCl_6, KCl, Li_2CO_3, NaCl, and Rb_2PtCl_6 in SnO_2
Rb	Cs_2PtCl_6, KCl, Li_2CO_3, NaCl, and Rb_2PtCl_6 in SnO_2
Re	Co_3O_4, $(NH_4)_2IrCl_6$, $(NH_4)_2OsCl_6$, $KReO_4$, and $(NH_4)_3RhCl_6 \cdot 1\frac{1}{2}H_2O$ in SnO_2
Rh	Co_3O_4, $(NH_4)_2IrCl_6$, $(NH_4)_2OsCl_6$, $KReO_4$, and $(NH_4)_3RhCl_6 \cdot 1\frac{1}{2}H_2O$ in SnO_2
Ru	$(NH_4)_2IrCl_6$, $(NH_4)_2OsCl_6$, and $(NH_4)_2[Ru(H_2O)Cl_5]$ in SnO_2

Table 10. (Continued)

Element Analyzed	Sample[a]
S	NaBr, NaCl, NaF, $NaHSO_3$, and NaI in SnO_2
Sb	Sb_2O_3 and SnO_2 in MgO
Sc	Sc_2O_3, V_2O_5, and Y_2O_3 in SnO_2
Se	As_2O_3, Bi_2O_3, Se, and SiO_2 in SnO_2
Si	AgCl, CuO, Fe_2O_3, and SiO_2 in ZnO
Sm	Sm_2O_3 in SnO_2
Sn	SnO_2 in Ag
Sr	$BaCO_3$, BeO, $CaCO_3$, MgO, and $SrSO_4$ in SnO_2
Ta	Cr_2O_3, MoO_3, Ta_2O_5, and WO_3 in SnO_2
Tb	Tb_4O_7 in SnO_2
Te	GeO_2, In_2O_3, Sb_2O_3, and TeO_2 in SnO_2
Th	ThO_2 in SnO_2
Ti	HfO_2, Nb_2O_5, TiO_2, and ZrO_2 in SnO_2
Tl	Tl_2SO_4 in SnO_2
Tm	Tm_2O_3 in SnO_2
U	UO_2 in SnO_2
V	Sc_2O_3, V_2O_5, and Y_2O_3 in SnO_2
W	WO_3 in SnO_2
Y	Sc_2O_3, V_2O_5, and Y_2O_3 in SnO_2
Yb	Yb_2O_3 in SnO_2
Zn	CdO, H_3BO_3, $Hg(C_2H_3O_2)_2$, and ZnS in SnO_2
Zr	HfO_2, Nb_2O_5, TiO_2, and ZrO_2 in SnO_2

in stannic dioxide, zinc oxide or magnesium oxide was used as a matrix material for silver, copper, iron, indium, antimony, and silicon. Oxygen and tin were examined in a sample of stannic dioxide in a silver matrix. The prepared samples ranged in concentration from 0.2 to 0.0001% or lower depending on the specific element.

Spectra for a given sample series were obtained for only the wavelength regions known (from the identification plates) to encompass the more intense lines of the element or elements being studied. The exposure period was about 3.5 minutes. The conditions utilized in exciting each element or group of elements are listed in Table 8. Because no background radiation appeared on the I-N or on portions of the II-F plates, these plates were pre-exposed (15 to 30 seconds) to an incandescent lamp in order to obtain an 85 to 90 percent transmission reading for the background radiation. This pre-exposing was carried out to make sure that the inertia of the photographic emulsion was exceeded thereby ensuring that the radiation from even the weakest line would be integrated by the emulsion.

Even the purest graphite powder available has residual impurities. Therefore, the spectrum of the most concentrated sample mixture was photographed in juxtaposition to spectra of the graphite and of the matrix material blended with the graphite. This was done both to facilitate the location of the lines of the analyte element and to determine the presence of any contamination or interferences from the matrix material or graphite. However, when pure graphite pellets were excited at pressures below atmospheric, the discharge tended to wander to the sides of the pellets. This problem was eliminated by sparking graphite pellets at atmospheric pressure.

B. Results

Table 11 lists the sensitive lines and corresponding estimated detection limits for 77 elements and gives available comparison data from various d.c. arc qualitative analysis schemes. The relative intensities of the sensitive lines resulting from excitation by a copper arc in air (76) were also included in Table 11 for comparison purposes. More sample ionization occurs under the high-energy spark excitation conditions used in this study than in a conventional d.c. arc discharge. The reader can convince himself of this fact by noticing that in several cases a lower detection limit is obtained for the ionized line of a given atom than for the neutral atom lines. With spark excitation, the strongest lines of about 20 elements corresponded to spectra of a higher degree of ionization than was reported by Meggers (76) for a d.c. arc. Several elements including cerium, chlorine, lanthanum, lutetium, phosphorus, sulfur, and thorium, number doubly-ionized lines among their most sensitive lines. This

Table 11. Most sensitive lines and detection limits in a helium atmosphere

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Ag	3382.89 I	3.7	0.00009[g]	2800	0.00005	0.0001	0.0001
7.6	3280.68 I	3.8	0.0002	5500			
	2413.18 II	10.2	0.0005	10			
	2437.79 II	9.9	0.0005[h]	8			

[a] Wavelengths and intensity ratings were taken from NBS Monograph 32-Part I (76). If the line was not listed in this source, the value quoted in the MIT Tables (37) is given. Other wavelength sources are indicated by appropriate footnotes.

[b] Energy level information was acquired from (in order of priority): Meggers *et al.* (76), Moore (84), or Zaidel *et al.* (122) unless indicated otherwise.

[c] % of element in matrix, diluted 1:2 with graphite.

[d] D.c. arc excitation in air (2). The question mark notation following several of Ahrens' detection limits were transcribed directly from his table.

[e] 20 A d.c. arc excitation in a 70% argon/30% oxygen atmosphere (22).

[f] 10 A d.c. arc excitation in air (1).

[g] A residual amount of the analyte element was present in the matrix material.

[h] Slight interference from coincident or adjacent spectral line.

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)^a	Excitation potential (eV)^b	Estimated detection limit (%)^c	Intensity NBS^a	Estimated detection limits		
					Ahrens %^{d}	deVilliers et al. %^{e}	Addink %^{f}
Al	3092.71 I	4.0	0.002	650	0.0002	0.0001	0.0002
6.0	3092.84 I	4.0					
	3944.03 I	3.1	0.006	450			
As	2860.44 I	6.6	0.006^g	90	0.01	0.01	0.002
9.8	2349.84 I	6.6	0.006^g	85			
	2959.70		0.009^g				
	2288.12 I	6.8	0.009	44			
	2745.00 I	6.8	0.009	44			
	3116.63 II		0.01				
	5651.53 II	12.3	0.01				
Au	2675.95 I	4.6	0.003	340	0.001	0.001	~0.0005
6.0	2427.95 I	5.1	0.004	200			
B	3451.41 II	12.6	0.0002		0.001	-	~0.0004
8.3	2497.73 I	5.0	0.0006	480			
	2496.78 I	5.0	0.0006	240			
Ba	4554.04 II	2.7	0.0002	6500	0.0005	0.0001	~0.0001
5.2	4934.09 II	2.5	0.0005	2000			
	6141.72 II	2.7	0.001	2000			
	6496.90 II	2.5	0.002	1200			
	4130.66 II	5.7	0.008	150			
	5853.68 II	2.7	0.008	280			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Be 9.3	3130.42 II	4.0	0.000008[g]	480	0.001	0.0001	~0.0001
	3131.07 II	4.0	0.000008	320			
	3321.34 I	6.4	0.001	100			
	3321.09 I	6.4	0.001	60			
	2348.61 I	5.3	0.002	300			
	2650.78 I	7.4	0.002	140			
Bi 7.3	3067.72 I	4.0	0.003[g]	3600	0.002	0.0001	~0.0003
	2897.98 I	5.7	0.006	400			
	3695.55		0.006				
	2855.67		0.006				
	2938.30 I	6.1	0.01	320			
	2989.03 I	5.6	0.01	280			
Br 11.8	4704.86 II	14.3[j]	0.02		-	-	-
	3540.1[i]		0.03				
	3506.5[i]		0.04				
	4785.50 II	14.2[j]	0.05				
	3517.4[i]		0.05				
	3562.4[i]		0.05				
	3333.0[i]		0.08				
	5182.36 II	14.6[j]	0.08				

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[i] Reference (69).

[j] Excitation energies were calculated from data in References (61) and (83).

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Ca	3933.67 II	3.2	<0.0002[g]	4200	0.0002	0.0001	~0.0001
6.1	3968.47 II	3.1	<0.0002[g,h]	2200			
	4226.73 I	2.9	0.0003	1100			
	3179.33 II	7.0	0.0006	50			
	3158.87 II	7.0	0.002	20			
	3736.90 II	6.5	0.002	15			
Cd	2288.02 I	5.4	0.002	1500	0.001	0.003	~0.001
9.0	2265.02 II	5.5	0.005	110			
	3610.51 I	7.4	0.008	360			
	2312.84 II	11.1	0.01	4			
	3403.65 I	7.4	0.01	80			
	3261.06 I	3.8	0.01	32			
Ce	3055.59 III[k]		0.006		0.05	-	-
1st-5.6	4186.6 II	3.8	0.01	250			
2nd-10.8	4133.80 II	3.9	0.01	190			
	3147.06 III[k]		0.01				
	3443.63 III[k]		0.01				
	3459.39 III[k]		0.01				
	3121.56 III[k]		0.01				
	3057.23 III[k]		0.01				

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[k] Reference (105).

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]		Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
						Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Cl 1st-13.0 2nd-23.8	4794.54	II	15.9	0.02		-	-	-
	4810.06	II	15.9	0.02				
	4253.51	II	18.8	0.04				
	4819.46	II	15.9	0.05				
	3602.10	III	25.0	0.05				
	8375.97	I	10.4	0.05				
Co 7.9	2388.92	II	5.6	0.0008	70	0.001	0.0003	0.0004
	2541.94	II	6.2	0.001	8			
	2580.33	II	6.0	0.002	40			
	3453.50	I	4.0	0.004	1300			
Cr 6.8	2677.16	II	6.2	0.0001	200	0.0001	0.0001	~0.0002
	3132.06	II	6.4	0.0002	75			
	3124.94	II	6.4	0.0002	60			
Cs 3.9	8521.10	I	1.4	0.01	1500	0.0002	-	-
	4603.76	II	10.1	0.01				
	5925.65		-	0.02				
	4277.10	II	-	0.02				
	5227.00	II	10.1	0.02				
Cu 7.7	3247.54	I	3.8	0.003[g]	5000	0.00005	0.0001	0.00008
	3273.96	I	3.8	0.004[g]	2500			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Dy 5.9	3531.70 II	3.5	0.004	2000	0.001	-	-
	3645.41 II	3.5	0.007	1000			
	4000.48 II	3.2	0.02	650			
	3536.03 II		0.02	500			
	3523.98 II	4.0	0.02	400			
Er 6.0	3692.64 II	3.4	0.01	700	0.001	-	-
	3372.76 II	3.7	0.02	750			
	3499.11 II	3.6	0.02	650			
	4007.97 I		0.05	1100			
	3830.53 II	3.2	0.05	320			
	3312.42 II	3.8	0.05	220			
Eu 5.7	4205.05 II	2.9	0.002	4000	0.001	-	-
	3819.67 II	3.2	0.002	3400			
	3930.48 II	3.4	0.002	2800			
	4129.70 II	3.0	0.002	2200			
	3971.96 II	3.3	0.003	2000			
	3724.94 II	3.3	0.003	1700			
	4435.56 II	3.0	0.005	900			
	3688.42 II	3.4	0.01	550			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
F	6856.02 I	14.4	0.09		-	-	-
17.4	6239.64 I	14.6	0.09				
	7754.70 I	14.5	0.1				
	6902.46 I	14.5	0.1				
	6348.50 I	14.6	0.1				
	7037.45 I	14.7	0.1				
	7398.68 I	14.3	0.1				
	3505.61 II	(28.5)	0.2				
Fe	2599.40 II	4.8	0.001[g]	200	0.0005	0.001	~0.0001
7.9	2611.87 II	4.8	0.001[g]	80			
	2739.55 II	5.5	0.001[g]	75			
	2585.88 II	4.8	0.001[g]	65			
	2598.37 II	4.8	0.001[g]	65			
	2382.04 II	5.2	0.001[g]	60			
	2395.62 II	5.2	0.001[g]	60			
	2749.32 II	5.5	0.001[g]	60			
	2631.05 II	7.5	0.001[g]	55			
	2613.82 II	4.8	0.001[g]	32			
	3734.87 I	4.2	0.001[g]	700			
	2617.62 II	4.8	0.001	32			
	2628.29 II	4.8	0.001	32			
	2727.54 II	5.6	0.001	18			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Ga 6.0	4172.06 I	3.1	0.002	2000	0.0003	-	~0.0005
	4032.98 I	3.1	0.004	1000			
	2943.64 I	4.3	0.004	950			
	2874.24 I	4.3	0.008	500			
Gd 6.2	3422.47 II	3.9	0.003	700	0.02?	-	-
	3646.19 II	3.6	0.01	600			
	3362.23 II	3.8	0.02	550			
	3768.39 II	3.4	0.02	850			
	3796.37 II	3.3	0.02	500			
	3545.80 II	3.6	0.02	440			
	3439.99 II	3.8	0.02	280			
	3463.98 II	4.0	0.02	280			
	3664.60 II		0.02	260			
	3671.20 II	3.4	0.02	200			
	3481.28 II	4.2	0.03	220			
Ge 7.9	2651.18 I	4.8	0.001	1200	0.0005	-	0.001
	2709.63 I	4.6	0.005	850			
	2754.59 I	4.6	0.005	650			
	2691.34 I	4.6	0.008	500			
	2651.58 I	4.6	0.01	550			
H 13.6	6562.82 I	12.0	0.4[g,1]		-	-	-

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[1] A blank of the analyte element was present in the spectrum of the supporting electrode material.

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Hf	3399.80 II	3.6	0.02	260	0.01?	-	~0.02
7	3505.23 II	4.6	0.02	140			
	3561.66 II	3.5	0.04	150			
	2773.36 II	5.2	0.04	110			
	3535.54 II	4.1	0.04	110			
	2975.88 II	4.8	0.04	100			
	3109.12 II	4.8	0.04	80			
	2751.81 II	5.5	0.05	40			
Hg	2536.52 I	4.9	0.002[h]	1500	0.01	-	~0.003
10.4	4358.35 I	7.7	0.004	400			
	3650.15 I	8.8	0.004	280			
	4046.56 I	7.7	0.01	180			
	5460.74 I	7.7	0.02	320			
	3125.66 I	8.8	0.02	40			
	3131.55 I	8.8	0.02	32			
	3131.83 I	8.8	0.02	32			
Ho	3456.00 II		0.003[h]	1800	0.001?	-	-
6.0	3398.98 II		0.006	900			
	3796.75 I		0.01	1000			
	3810.73 I		0.01	1000			
	3484.84 II		0.01	700			
	3425.34 II		0.01	200			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
I	3940.24		0.02		-	-	-
10.4	3055.37 II	18.3^{m}	0.04				
	3931.01		0.04				
	3498.03		0.05				
	5338.19 II	13.9^{m}	0.05				
	5161.19 II	12.4^{m}	0.08				
	3481.83		0.09				
	4220.96 II		0.09				
	5464.62 II	12.3^{m}	0.09				
In	4101.76 I	3.0	0.002	1700	0.0001	-	~0.001
5.8	3256.09 I	4.1	0.002	1300			
	4511.31 I	3.0	0.003	1800			
	3258.56 I	4.1	0.004	300			
Ir	3133.32 I	4.7	0.08	340	0.005	-	~0.04
9	2924.79 I	4.2	0.1	320			
	3220.78 I	4.2	0.2	500			
	3513.64 I	3.5	0.2	320			
	2694.23 I	5.0	0.2	220			
	2943.15 I	5.0	0.2	200			

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[m] Reference (71).

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)^a	Excitation potential (eV)^b	Estimated detection limit (%)^c	Intensity NBS^a	Estimated detection limits Ahrens %^{d}	deVilliers et al. %^{e}	Addink %^{f}
K 4.3	7664.91 I	1.6	0.001	1800	0.0002	0.03	~0.3
	7698.98 I	1.6	0.001	900			
	4186.23 II	23.1	0.01				
	4044.14 I	3.1	0.02	32			
La 1st-5.6 2nd-11.4	3171.68 III	5.8	0.002	20	0.001	-	~0.004
	3949.10 II	3.5	0.006^h	900			
	3517.14 III	5.2	0.006	10			
	3794.78 II	3.5	0.01	460			
	4123.23 II	3.3	0.01	440			
	4086.72 II		0.02	550			
Li 5.4	6707.84 I	1.8	0.0008	3600	0.0001	-	~0.004
	6103.64 I	3.9	0.001	320			
	3232.61 I	3.8	0.005	17			
	4602.86 I	4.5	0.01	13			
	8126.52 I	3.4	0.02	48			
Lu 1st-~5 2nd-13.9	3554.43 II	5.6	0.002	280	0.001?	-	-
	3397.07 II	5.1	0.002	240			
	2603.33 III	5.5	0.002	38			
	2772.58 III	5.5	0.002	26			
	3057.90 III	4.8	0.002	9			
	2615.42 II	4.7	0.002	1200			
	3077.60 II	5.6	0.002	500			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Lu (cont.)	2911.39 II	6.0	0.003	600			
	3507.39 II	3.5	0.003	480			
	3020.54 II	5.6	0.003	200			
	3254.31 II	5.6	0.004	280			
Mg 7.6	2795.53 II	4.4	<0.00002[g]	1000	0.0002	0.0001	0.00004
	2802.70 II	4.4	<0.00002[g]	600			
	2798.06 II	8.9	0.00002	16			
	2852.13 I	4.3	0.0001	6000			
	2790.79 II	8.9	0.0002	13			
Mn 7.4	2576.10 II	4.8	0.0002	1200	0.001	0.001	~0.00015
	2949.20 II	5.4	0.0002	240			
	2605.69 II	4.8	0.001	550			
	2939.30 II	5.4	0.002	190			
	2933.06 II	5.4	0.002[h]	140			
	3441.99 II	5.4	0.002	110			
	2593.73 II	4.8	0.003	800			
Mo 7.1	2816.15 II	6.1	0.001	220	0.0005	0.001	~0.003
	2775.40 II	6.1	0.002	220			
	2871.51 II	5.8	0.002	220			
	2923.39 II	5.8	0.002	160			
	3132.59 I	4.0	0.002	1800			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)^a	Excitation potential (eV)^b	Estimated detection limit (%)^c	Intensity NBS^a	Estimated detection limits		
					Ahrens %^{d}	deVilliers et al. %^{e}	Addink %^{f}
Mo (cont.)	2930.50 II	5.7	0.002	140			
	2684.14 II	6.3	0.002	110			
	3087.62 II	7.4	0.002	34			
	3292.31 II	6.9	0.002	24			
	3635.14 II	6.6	0.002	3.5			
	3692.64 II	6.4	0.002	20			
N (CN)	bandheads						
	3871.4		0.002		-	-	-
	3883.4		0.04				
Na 5.1	5895.92 I	2.1	0.0001^g	1000	0.00005	0.001	~0.0001
	3302.32 I	3.8	0.008	30			
	3302.99 I	3.8	0.008	15			
	8194.81 I	3.6	0.01	220			
	8183.27 I	3.6	0.02	110			
Nb 6.9	3130.79 II	4.4	0.006	180	0.003	-	~0.01
	3659.61 II	5.3	0.009	24			
	2950.88 II	4.7	0.01	170			
	3163.40 II	4.3	0.01	140			
	3194.98 II	4.2	0.01	120			
	3094.18 II	4.5	0.02	220			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Nd	4012.25 II	3.7	0.04	220	0.001	-	-
5.5	4061.09 II	3.5	0.05	280			
	3863.40 II	3.2	0.05	220			
	4109.46 II	3.3	0.08	150			
	4156.08 II	3.2	0.09	180			
Ni	3524.54 I	3.5	0.006	750	0.0005	0.0001	0.0002
7.6	3414.76 I	3.6	0.008	750			
	2394.52 II	6.8	0.008	12			
	2416.14 II	7.0	0.008	10			
	2316.04 II	6.4	0.008	7			
	3461.65 I	3.6	0.008	460			
	3002.49 I	4.2	0.008	320			
O	7771.93 I	10.7	0.4[g,1]		-	-	-
13.6	7774.14 I	10.7	0.4[g,1]				
	7775.43 I	10.7	0.8[g,1]				
Os	3042.74 II	5.5	0.01	12	0.005	-	-
8.7	3213.31 II	5.5	0.01[h]	16			
	2255.85 II	5.5	0.05	19			
	2336.80 II	5.7	0.05	17			
	2580.03 II	6.4	0.05	12			
	3301.56 I	3.8	0.05	800			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
P 1st-10.5 2nd-19.7	2535.65 I	7.2	0.003	60	0.01?	-	0.002
	2553.28 I	7.2	0.01	38			
	4222.15 III	17.5	0.01				
	3233.61 III	21.3	0.01				
	6043.05 II	12.8	0.02				
	2554.93 I	7.2	0.04	15			
	4059.27 III	17.5	0.04				
	4246.88 III	17.4	0.04				
Pb 7.4	3683.48 I	4.3	0.001	1400	0.0005	0.001	~0.0003
	4057.83 I	4.4	0.002	3400			
	3639.58 I	4.4	0.002	550			
	2833.06 I	4.4	0.003	950			
	2801.99 I	5.7	0.004	1000			
Pd 8.3	3404.58 I	4.4	0.002	2600	0.001	-	-
	3634.70 I	4.2	0.003	2200			
	3421.24 I	4.6	0.003	1400			
	2488.92 II	8.1	0.004	8			
	3516.94 I	4.5	0.004	1300			
	3553.08 I	4.9	0.004	1300			
	3481.15 I	4.8	0.004	1100			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Pr 5.4	4100.75 II	3.6	0.01	260	0.001	-	-
	4143.14 II	3.4	0.01	240			
	4008.71 II	3.7	0.01	170			
	3816.17 II		<0.02[h]	140			
	4179.42 II	3.2	0.02	460			
	4222.98 II	3.0	0.02	340			
	4225.33 II	2.9	0.02	340			
	4189.52 II	3.3	0.02	220			
	2980.52		0.02				
	3367.53		0.02				
Pt 9.0	3064.71 I	4.0	0.003	320	0.005	-	~0.0008
	2702.40 I	4.7	0.02	200			
	2733.96 I	4.6	0.02	180			
	2997.97 I	4.2	0.02	180			
	2774.78 II		0.02				
	2794.21 II	6.1	0.02	1.6			
	2929.79 I	4.2	0.02	170			
	2719.04 I	4.7	0.02	130			
	3042.64 I	4.2	0.02	80			
Rb 4.2	7800.23 I	1.6	0.005	3000	0.0001	-	-
	4244.44 II		0.02				

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Re 7.9	3460.46 I	3.6	0.009	5500	0.01	-	-
	2733.04 II	6.7	0.01	55			
	3464.73 I	3.6	0.02	4000			
	3580.15 II	5.6	0.02	80			
	2461.84 II		0.02	65			
	2502.35 II	7.6	0.02	46			
Rh 7.5	2490.77 II	7.1	0.003	8	0.001	-	-
	3434.89 I	3.6	0.005	700			
	3692.36 I	3.4	0.006	800			
	3502.52 I	3.5	0.006	500			
	2415.84 II	7.6	0.009	4			
	2520.53 II	7.0	0.01	10			
	2461.04 II	7.3	0.01	7			
	2910.17 II	7.4	0.01	5			
	3528.02 I	3.7	0.01	750			
Ru 7.4	2678.76 II	5.8	0.002	75	0.001	-	-
	2456.57 II	6.3	0.003	40			
	2692.06 II	5.9	0.006	36			
	2734.35 II	5.8	0.006	34			
	2976.59 II	6.6	0.006	15			
S 1st-10.4 2nd-23.4	3497.34 III		0.05		-	-	-
	4142.29 II	18.8	0.05				
	4145.10 II	18.8	0.05				
	4162.70 II	18.8	0.05				

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
S (cont.)	5453.81 II	15.9	0.08				
	3632.02 III[n]	21.1	0.09				
	3717.78 III[n]	21.5	0.09				
Sb 8.6	2598.05 I	5.8	0.006	600	0.002	0.01	0.002
	3267.51 I	5.8	0.01	85			
	3504.47 I	5.8	0.01				
	2669.64		0.02				
	3232.52 I	6.1	0.02	100			
Sc 1st-6.5 2nd-12.8	3613.84 II	3.4	0.0002	2500	0.0002	-	-
	3630.75 II	3.4	0.0002	1800			
	4246.83 II	3.2	0.0005	1400			
	3642.79 II	3.4	0.0005	1200			
	2699.11 III	7.8	0.001	5			
	3645.31 II	3.4	0.001	600			
	3651.80 II	3.4	0.001	480			
	4314.09 II	3.5	0.002	380			
	3368.95 II	3.7	0.002	360			

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[n] Reference (84).

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Se	3544[o]		0.009		-	-	-
9.8	3738.7[o]		0.009				
	3387.2[o]		0.01				
	3637.5[o]		0.01[h]				
	5227.51		0.03				
	3711.6[o]		0.04				
Si	2881.60 I	5.1	0.002[g]	260	0.002	0.003	0.0002
8.2	2524.11 I	4.9	0.006[g]	240			
	2528.51 I	4.9	0.006[g]	200			
	3905.53 I	5.1	0.008	11			
Sm	3592.60 II	3.8	<0.05[g]	350	0.05?	-	-
5.6	3568.27 II	4.0	0.02	350			
	3634.29 II	3.6	0.02	280			
	3885.29 II	3.7	0.05	280			
	4424.34 II	3.3	0.05	200			
	3661.36 II	3.4	0.05	180			
	3670.84 II	3.5	0.05	180			
	3306.39 II	4.2	0.06	140			

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[o] Reference (122).

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Sn	2839.99 I	4.8	0.002	1400	0.001	0.001	0.001
7.3	2863.33 I	4.3	0.002	1000			
	3034.12 I	4.3	0.006	850			
	3009.14 I	4.3	0.008	700			
	3262.34 I	4.9	0.02	550			
	3801.02 I	4.3	0.02	280			
Sr	4077.71 II	3.0	<0.0001	4600	0.0005	0.0001	~0.02
5.7	4215.52 II	2.9	0.0003	3200			
	3464.46 II	6.6	0.002	95			
	3380.77 II	6.6	0.005	65			
	4607.33 I	2.7	0.007	650			
	4305.45 II	5.9	0.008	34			
Ta	2685.17 II	5.1	0.01[h]	180	0.01?	-	-
7.9	2635.58 II	4.8	0.01	140			
	2400.63 II	5.9	0.02	140			
	2675.90 II	5.2	0.02	90			
	2603.49 II	5.5	0.02	70			
Tb	3509.17 II		0.003	600	0.001	-	-
(5.8)	3561.74 II		0.006	340			
	3702.85 II		0.01	460			
	3676.35 II		0.01	380			
	3650.40 II		0.01	240			
	3703.92 II		0.01	240			
	3523.66 II		0.01	140			
	3293.07 II		0.02	160			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Tb	3874.19 II		0.02	320			
(cont.)	3568.51 II		0.02	440			
	3324.40 II		0.02	400			
	3848.76 II		0.02	340			
	3899.20 II		0.02	220			
	3658.88 II		0.02	200			
	3568.51 II		0.02	170			
	2891.41 II		0.02	-			
	3682.26 II		0.02	80			
	3939.52 II		0.02	75			
Te	2385.76 II[p]		0.02		0.02	-	-
9.0	2858.29 II[p]		0.02				
	3251.37		0.02				
	2383.25 II[p]		0.03				
	3277.50		0.06				
	3278.77		0.06				
	5708.12 II[p]		0.06				
Th	2978.72 III[q]		0.01		0.01	0.01	-
1st-?	3221.29 II		0.01	40			
2nd-?	3216.63 III[q]		0.02				
	3291.74 II	4.5	0.04	65			
	3301.26 II		0.04	17			

[p] Reference (36).

[q] Reference (123).

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]		Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
						Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Th (cont.)	3131.07	II	4.0	0.04	11			
	3377.48	III[a]		0.05[h]				
	3232.04	III[a]		0.05				
	3148.06	III[a]		0.05				
	3097.96	III[a]		0.05				
	2899.72	II	5.0	0.05	22			
Ti 6.8	3349.41	II	3.7	0.0008	1000	0.001	0.0003	~0.001
	3234.52	II	3.9	0.0008	550			
	3341.88	II	4.3	0.0008	480			
	3078.64	II	4.0	0.0008	190			
	3372.80	II	3.7	0.001	480			
	3383.76	II	3.7	0.001	480			
	3239.04	II	3.8	0.001	340			
	3088.02	II	4.1	0.001	300			
	3759.30	II	3.9	0.001	280			
	3685.20	II	4.0	0.001	260			
	3322.94	II	3.9	0.002	240			
	3761.32	II	3.9	0.002	240			
	3241.99	II	3.8	0.002	220			
	3075.22	II	4.0	0.002	130			
	3066.22	II	4.0	0.002	110			
	3252.91	II	3.8	0.002	100			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Tl 6.1	3519.24 I	4.5	0.0006	2000	0.0001	-	0.007
	3091.66 II		0.004				
	5350.46 I	3.3	0.008	1800			
	3775.72 I	3.3	0.008[h]	1200			
	3529.43 I	4.5	0.008	500			
	2767.87 I	4.5	0.008	400			
	3229.75 I	4.8	0.008	120			
Tm 6.2	3462.20 II	3.6	0.002	800	0.001?	-	-
	3425.08 II	3.6	0.002	600			
	3848.02 II	3.2	0.003	750			
	3131.26 II	4.0	0.003	700			
	3761.33 II	3.3	0.005	500			
	3453.67 II	3.6	0.005	460			
	3761.91 II	3.3	0.005	400			
U ~4	3670.07 II	3.5	0.05	160	0.01	0.03	-
	4090.14 II	3.2	0.05	160			
	2651.84		0.05				
	3037.91		0.05				
	3985.80 II	3.8	0.08	85			
	4241.67 II	3.5	0.08	75			
	3013.83		0.08				

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
V 6.7	3093.11 II	4.4	0.0002	500	0.0005	0.001	~0.002
	3102.30 II	4.4	0.0002	400			
	3110.71 II	4.3	0.0002	340			
	2924.02 II	4.6	0.0005	320			
	3118.38 II	4.3	0.002	260			
	2924.64 II	4.6	0.002	220			
	3125.28 II	4.3	0.002	200			
	2687.96 II	4.6	0.002	140			
	3271.12 II	4.9	0.002	120			
W 8.0	2397.09 II	5.6	0.02	34	0.002	-	-
	2702.11 II	6.2	0.02	20			
	4008.75 I	3.4	0.05	950			
	2764.27 II	4.5	0.05	50			
	2697.71 II	4.8	0.05	26			
	2579.54 II	5.7	0.05	20			
	2722.81 II	6.4	0.05	20			
	3077.52 II		0.05	14			
Y 1st-6.4 2nd-12.2	3710.30 II	3.5	0.0005[g]	1500	0.001	-	-
	3774.33 II	3.4	0.0005[g]	1200			
	3600.73 II	3.6	0.0008	1300			
	3633.12 II	3.4	0.0008	1000			
	4374.94 II	3.2	0.001	1200			
	3788.70 II	3.4	0.001	850			
	3601.92 II	3.5	0.001	800			
	2414.68 III	5.1	0.002	16			
	3611.05 II	3.6	0.002	1000			

Table 11. (Continued)

Element & ionization potential (eV)	Sensitive lines (Å)[a]	Excitation potential (eV)[b]	Estimated detection limit (%)[c]	Intensity NBS[a]	Estimated detection limits		
					Ahrens %[d]	deVilliers et al. %[e]	Addink %[f]
Y (cont.)	4177.54 II	3.4	0.002	800			
	3327.89 II	4.1	0.002	600			
	3195.62 II	4.0	0.002	300			
	2945.94 III	5.1	0.002	32			
Yb 6.2	3694.19 II	3.4	<0.004[h]	3200	0.001	-	-
	3289.37 II	3.8	0.003	2600			
	3987.98 I	3.1	0.006	1900			
	2891.38 II	4.3	0.006	500			
	2970.56 II	4.2	0.008	280			
	2818.72 III[r]		0.01				
Zn 9.4	3345.02 I	7.8	0.005[h]	140	0.01	0.003	~0.003
	2502.00 II	11.0	0.005				
	3302.59 I	7.8	0.005	90			
	2557.96 II	11.0	0.01				
	4810.53 I	6.6	0.02	140			
	4722.16 I	6.6	0.02	100			
	2770.98 I	8.5	0.02	6			
	6362.35 I	7.7	0.02	12			
Zr 6.8	3438.23 II	3.7	0.002	750	0.001	0.001	-
	3496.21 II	3.6	0.002	650			
	3556.60 II	4.0	0.006	340			
	3481.15 II	4.4	0.006	200			
	3479.39 II	4.3	0.006	190			
	3273.05 II	4.0	0.006	160			
	3430.53 II	4.1	0.009	160			
	3698.17 II	4.4	0.009	120			

[r] Reference (17).

greater degree of ionization is both an advantage and a disadvantage. The more energetic source permits the excitation of the sensitive ion lines of the halogens that are located in the visible wavelength region. However, the other elements are also ionized and in general the principal spectral lines of ionized atoms have shorter wavelengths than the intense lines of neutral atoms. Consequently, the most sensitive lines of some of the ionized atoms may be located at wavelengths less than 2200 Å.

In most cases, the reported estimated detection limit was the lowest concentration in which the sensitive lines were visually detected. However, when the matrix material or graphite supporting material was contaminated with a residual amount of the analyte element, the reported detection limit was the lowest concentration at which there was a noticeable change in the intensity of the line. These detection limits correspond to the concentration, % by weight, of analyte element in the matrix material. The uncertainty in these reported values is estimated to be 50%. The detection limits of the other investigators listed in Table 11 are based on total sample composition. Consequently, the detection limits reported in this study would be lowered to 1/3 of the stated values if the concentration were expressed in terms of the total capped pellet composition. One should keep these facts in mind when comparing the detection limits listed in Table

11. Comparison with the arc methods indicates that spark excitation provides detection limits that are equivalent or better for 51 of 68 elements and in addition permits the detection of hydrogen, nitrogen, oxygen, sulfur, selenium, fluorine, chlorine, bromine, and iodine.

As a group, the alkaline earth ions have exceptionally low detection limits. Unfortunately, because of a large amount of residual calcium in the matrix material, it was not possible to report an actual detection limit. In their singly ionized form, these elements have only one s electron in the unfilled shells and this configuration has a relatively low stability. As a result, the energy of the first excited state is relatively low and therefore easily excited. Usually, the transition probabilities for the $s \rightleftarrows p$ transitions in ions with the alkali metal configuration, are generally high. Meggers (74) states that the most intense line of a spectrum, the raie ultime, "originates with a simple interchange of a single electron between s and p states, usually preferring configurations in which only one electron occurs in such states". Consequently, the ion lines of these elements should be easily excited and quite intense.

Similar considerations help to explain the poor detectability of aluminum, gallium, indium, and thallium. The ionic configurations of these elements consist of a filled s subshell which is quite stable. Consequently, the excited states are very high in energy and the strongest ionic lines lie in the far ultraviolet (75). Thus, for the detection of these elements, it is necessary to utilize lines emitted from the less populated (under these excitation conditions) energy levels of the neutral atom. Consequently, the intensity of these lines are correspondingly lowered.

The detection limits of the alkali metals are also relatively poor. The singly ionized form of these elements possess the very stable s^2 p^6 (noble gas) configuration. As a consequence, the most sensitive ion lines of these elements are located below 2200 Å. Thus, as in the previous case, the less sensitive (under these excitation conditions) atom lines must be used.

Because of the difficulty in obtaining a matrix material free of copper, iron, silicon, hydrogen, and oxygen, the actual detection limits of these elements are undoubtedly significantly lower than the estimated values. A blank of oxygen and hydrogen was also found in the spectrum of pure graphite pellets. The source of this contamination may arise from several sources including the adsorption of water vapor on the graphite powder, the adsorption of oxygen on the surfaces of the excitation chamber, or contamination in the helium supply. Successive sparking (or arcing between two sparking periods) of the graphite pellets removed the majority of the hydrogen blank but had little effect on the intensity of the oxygen lines. This indicates that most of the hydrogen blank is from the graphite and not from the helium.

When silver pellets containing various concentrations of carbon in a stannic oxide matrix were excited, the intensity of the carbon lines in the resulting spectra remained essentially constant even though the carbon concentration changed. It was possible to differentiate between 3 and 0.8% carbon, but not between lower concentrations. The spectrum of pure silver pellets indicated the presence of a high carbon blank in the silver powder. Because of the preceding difficulties and because this was the only element that could not be analyzed in graphite pellets, the investigation of carbon was discontinued.

C. Practical Considerations

One disadvantage of the arcing or sparking of graphite electrodes in an air atmosphere is the resulting formation of cyanogen bands which obscure the 3600 to 4200 Å spectral region. This interference was eliminated by replacing air (N_2) with helium. However, if the unknown sample contains nitrogen and is in a graphite electrode, cyanogen bands will again form. This is, indeed, a very sensitive way to detect nitrogen, however, major amounts of nitrogen will also interfere with the identification of some of the other elements.

Another difficulty encountered involves the sparking of pellets containing hydrated salts. Pellets of samples containing absorbed or combined water may be shattered at the initial spark contact because of the sudden vaporization of the water. This problem is often encountered in arc and spark excitation. To avoid this difficulty the recommended procedure is to heat the sample before the analysis in order to drive off any absorbed water or water of crystallization. However, such a procedure is unsatisfactory if the detection of water of hydration is of interest. In addition, prior heating may result in the loss of some other volatile constituents. If sufficient sample is available, two analyses are advisable, one with and one without prior heating.

VIII. SUGGESTIONS FOR FUTURE INVESTIGATIONS

An obvious extension of this method would be the preparation of a "master spectrum". This composite spectrum should be composed of a few of the most prominent lines of each element. Such a "master spectrum" would simplify the identification of unknowns. Because of the complexity of the spectra of the rare earths and some of the transition elements, it would probably be desirable to prepare several "master spectra".

Since low detection limits for the halogens have been obtained from hollow cathode excitation, explorations on the application of this excitation source to a qualitative analysis method are also of interest.

IX. SUMMARY

A spectrographic qualitative analysis scheme which in principle allows the detection of all elements except helium in a sample was developed. This scheme is based on the excitation of the sample in conducting briquettes by a high-voltage spark in a helium atmosphere. Under these excitation conditions the detection limits for the halogens and sulfur are in the range of 0.02 to 0.09%. The elements oxygen and hydrogen can be estimated down to 0.4%, while nitrogen can be detected down to 0.002%. The detection limits for the alkaline earth elements range from less than 0.000008 to 0.0002% and for the alkali metals from 0.001 to 0.01%. With the exception of hafnium, tungsten, iridium, tellurium, uranium, neodymium, and samarium the remaining elements had detection limits of 0.01% or less. Thus, this qualitative analysis scheme encompasses, for the first time, the detection of the halogens, sulfur, selenium, oxygen, nitrogen, and hydrogen along with all of the metallic elements.

X. LITERATURE CITED

1. Addink, N. W. H., Spectrochim. Acta, 11, 168 (1956).

2. Ahrens, L. H. Wavelength tables of sensitive lines. Reading, Massachusetts, Addison-Wesley Publishing Co., Inc. 1951.

3. Andermann, G. and J. W. Kemp, Am. Soc. Testing Mater., Spec. Tech. Publ., 259, 23 (1959).

4. Andrychuk, D. and C. E. Jones, Jr., Ultrapurif. Semicond. Water Conf., Boston, Massachusetts, Proc., 1961, 373 (1962).

5. Azevedo, L. H., A. W. Specht, and R. S. Harner, Spectrochim. Acta, 6, 331 (1954).

6. Balloffet, G. and J. Romand, J. Phys. Radium, 16, 490 (1955).

7. Balloffet, G., J. Romand, and B. Vodar, Colloq. Spectroscopicum Intern. Proc., 8th, 112 (1959).

8. Bardocz, A., Colloq. Spectroscopicum Intern. Proc., 9th 2, 144 (1961).

9. Berezin, I. A., Ind. Lab. (USSR), 27, 862 (1961).

10. Berezin, I. A. and K. V. Aleksandrovich, J. Anal. Chem. USSR, 16, 604 (1961).

11. Berezin, I. A., O. F. Degtyareva, and P. P. Shevchenko, Zh. Prikl. Spektroskopii, Akad. Nauk Belorussk. SSR, 4 (2), 170 (1966).

12. Berezin, I. A. and G. N. Yanovskaya, Opt. Spectr. (USSR), 14, 11 (1963).

13. Birks, F. T., Spectrochim. Acta, 6, 169 (1954).

14. Borovik, S. A., Izv. Akad. Nauk SSSR, Ser. Fiz., 14, 630 (1950). Original not available; abstracted in Chem. Abstr., 44, 10592 (1950).

15. Boumans, P. W. J. M. Theory of spectrochemical excitation. London, England, Hilger and Watts, Ltd. 1966.

16. Brown, S. C. Introduction to electrical discharges in gases. New York, New York, John Wiley and Sons, Inc. 1966.

17. Bryant, B. W., J. Opt. Soc. Am., 55, 771 (1965).

18. Buffereau, M., G. Crehange, and J. Poublan, U.S. Atomic Energy Commission Report, CEA-R 2436 [France. Commissariat a l'Energie Atomique. Centre d'Etudes Nucleaires, Saclay], (1964).

19. Burrows, K. M. and J. F. Horwood, Spectrochim. Acta, 19, 17 (1963).

20. Contamin, G., U.S. Atomic Energy Commission Report, CEA-R-2826 [France. Commissariat a l'Energie Atomique. Centre d'Etudes Nucleaires, Saclay], (1965).

21. Cundall, C. M. and J. D. Craggs, Spectrochim. Acta, 7, 149 (1955).

22. deVilliers, D. B., D. van Wamelen, and A. Strasheim, Appl. Spectry., 20, 298 (1966).

23. Dieke, G. H., Am. Soc. Testing Mater., Spec. Tech. Publ., 76, 1 (1948).

24. Enns, J. H. and R. A. Wolfe, Am. Soc. Testing Mater., Spec. Tech. Publ., 76, 12 (1948).

25. Enns, J. H. and R. A. Wolfe, J. Opt. Soc. Am., 39, 298 (1949).

26. Falk, H., Spectrochim. Acta, 21, 423 (1965).

27. Feldman, C. and J. Y. Ellenburg, Spectrochim. Acta, 7, 349 (1956).

28. Fizalkowski, J. and O. Szczerbinska, Colloq. Spectroscopicum Intern. Proc., 8th, 191 (1959).

29. Fizalkowski, J. and A. Zelle, Polska Akad. Nauk, Inst. Badan Jadrowych, Report, 176/XIII (1960).

30. Fowler, R. G. and R. A. Wolfe, J. Opt. Soc. Am., 35, 170 (1945).

31. Gatterer, A., Spectrochim. Acta, 3, 214 (1948).

32. Gillieson, A. H. and F. T. Birks, Congr. Group. Avan. Methodes Anal. Spectrog. Prod. Met., 14, 155 (1951).

33. Gillis, J., J. Eeckhout, and N. Kemp, Rev. Universelle Mines, 8, 284 (1952).

34. Griem, H. R. Plasma spectroscopy. New York, New York, McGraw-Hill Book Co., Inc. 1964.

35. Gunn, E. L., Anal. Chem., 26, 1815 (1954).

36. Handrup, M. B. and J. E. Mack, Physica, 30, 1245 (1964).

37. Harrison, G. R., ed. MIT wavelength tables. New York, New York, John Wiley and Sons, Inc. 1939.

38. Harrison, G. R., R. C. Lord, and J. R. Loofbourow. Practical spectroscopy. New York, New York, Prentice-Hall, Inc. 1948.

39. Harvey, C. E. and J. W. Mellichamp, Anal. Chem., 33, 1242 (1961).

40. Hasler, M. F. and H. W. Dietert, J. Opt. Soc. Am., 33, 218 (1943).

41. Hasted, J. B. Physics of atomic collisions. Washington, D.C., Butterworths. 1964.

42. Hedfeld, K., Z. Physik, 68, 610 (1931).

43. Hellund, E. J. The plasma state. New York, New York, Reinhold Publishing Corp. 1961.

44. Honma, M., Anal. Chem., 27, 1656 (1955).

45. Huang, Pung-li, Ind. Lab. (USSR), 24, 390 (1958).

46. Hurd, W. G. Terminal report for Spectrochemistry Group I, Ames Laboratory. Ames, Iowa, Institute for Atomic Research, U.S. Atomic Energy Commission. 1956.

47. Jaffe, H. W., Am. Mineralogist, 34, 667 (1949).

48. Jarrell, R. F. Excitation units. In Clark, G. L., ed. The encyclopedia of spectroscopy. Pp. 158-169. New York, New York, Reinhold Publishing Corp. 1960.

49. Johnson, A. J. and E. Vejvoda, Appl. Spectry., 20, 262 (1966).

50. Johnson, W. W. A. and D. P. Norman, Ind. Eng. Chem., Anal. Ed., 15, 119 (1943).

51. Jones, F. L., J. Soc. Chem. Industry, 64, 317 (1945).

52. Kaiser, H. and A. Wallraff, Ann. Physik, Series 5, 34, 297 (1939).

53. Kaiser, H. and A. Wallraff, Z. Physik, 112, 215 (1939).

54. Keller, R. E. and L. Smith, Anal. Chem., 24, 796 (1952).

55. Kibisov, G. I., Zh. Analit. Khim., 5, 51 (1950).

56. Kibisov, G. I., S. V. Knyazeva, and M. G. Tarakanova, Zavodsk. Lab., 13, 1493 (1947). Original not available; abstracted in Chem. Abstr., 43, 4179 (1949).

57. Koehler, M., Congr. Group. Avan. Methodes Anal. Spectrog. Prod. Met., 18, 215 (1955).

58. Korovin, Yu. I., Ind. Lab. (USSR), 31, 46 (1965).

59. Korovin, Yu. I., J. Anal. Chem. USSR, 15, 707 (1960).

60. Kudymov, B. Y., V. I. Malinina, and V. P. Varlamov, Ind. Lab. (USSR), 25, 608 (1959).

61. Lacroute, P., Ann. Physik, Series 11, 3, 5 (1935).

62. Lemieux, P. E. and R. H. Black, Anal. Chem., 32, 246 (1960).

63. Levintov, I. I., Izv. Akad. Nauk SSSR, Ser. Fiz., 9, 699 (1945).

64. Levintov, I. I., Zh. Tekhn. Fiz., 17, 795 (1947).

65. Loeb, L. B. Fundamental processes of electrical discharge in gases. New York, New York, John Wiley and Sons, Inc. 1939.

66. MacDonald, A. D. Microwave breakdown in gases. New York, New York, John Wiley and Sons, Inc. 1966.

67. McNally, J. R., G. R. Harrison, and E. Rowe, J. Opt. Soc. Am., 37, 93 (1947).

68. Mandelstam, S. L., Spectrochim. Acta, 15, 255 (1959).

69. Mandelstam, S. L. and S. M. Raiski. Tablicy spektralnych linij. Gos. Obied. Nauczno-Tiechn. Izd., NKTP SSSR, Moskwa. 1938. Original not available; cited in Fizalkowski, J. and A. Zelle, Polska Akad. Nauk, Inst. Badan Jadrowych, Report, 176/XIII, (1960).

70. Mansfield, W. O., J. C. Fuhrmeister, and D. L. Fry, J. Opt. Soc. Am., 41, 412 (1951).

71. Martin, W. C. and C. H. Corliss, J. Res. Nat. Bur. Std., 64A, 443 (1960).

72. Marzuvanov, V. L., Vestn. Akad. Nauk Kaz. SSR, 16, 85 (1960).

73. Massey, H. S. W. and E. H. S. Burhop. Electronic and ionic impact phenomena. Oxford, England, Clarendon Press. 1952.

74. Meggers, W. F., J. Opt. Soc. Am., 31, 39 (1941).

75. Meggers, W. F., J. Opt. Soc. Am., 31, 605 (1941).

76. Meggers, W. F., C. H. Corliss, and B. F. Scribner, National Bureau of Standards Monograph, 32, Part 1, (1961).

77. Melamed, J., U.S. Atomic Energy Commission Report, CEA-1999 [France. Commissariat a l'Energie Atomique. Centre d'Etudes Nucleaires, Saclay], (1961).

78. Mellichamp, J. W. Nonmetallic elements. In Clark, G. L., ed. The encyclopedia of spectroscopy. Pp. 230-242. New York, New York, Reinhold Publishing Corp. 1960.

79. Milazzo, G., Appl. Spectry., 21, 185 (1967).

80. Milazzo, G. and N. Sopranzi, Appl. Spectry., 21, 172 (1967).

81. Milazzo, G. and N. Sopranzi, (Italy) Superior Inst. of Health Report AD-431066. 1963.

82. Mochalov, K. N. and E. L. Raff, Soviet Phys.-Tech. Phys., 1, 487 (1957).

83. Moore, C. E., National Bureau of Standards Circular, 467, Vol. 2, (1949).

84. Moore, C. E., National Bureau of Standards Technical Note, 36 (Rev. ed.), (1959).

85. Nachtrieb, N. H. Principles and practice of spectrochemical analysis. New York, New York, McGraw-Hill Book Co., Inc. 1950.

86. Olsen, H. N. and W. S. Huxford, Phys. Rev., 87, 922 (1952).

87. Ornstein, L. S. and H. Brinkman, Physica, 1, 797 (1934).

88. Papish, J., L. E. Hoag, and W. E. Snee, Ind. Eng. Chem., Anal. Ed., 2, 263 (1930).

89. Pfeilsticker, K., Microchim. Acta, 2/3, 358 (1955).

90. Pfeilsticker, K., Spectrochim. Acta, 1, 424 (1940).

91. Prokof'ev, V. K., Izv. Akad. Nauk SSSR, Ser. Fiz., 9, 691 (1945).

92. Reinold, F. and E. Schroll, Z. Anal. Chem., 190, 410 (1962).

93. Rollwagen, W., Spectrochim. Acta, 1, 65 (1939).

94. Romand, J., G. Balloffet, and B. Vodar, Colloq. Spectroscopicum Intern. Proc., 8th, 160 (1959).

95. Romand, J., G. Balloffet, and B. Vodar, Spectrochim. Acta, 15, 454 (1959).

96. Russell, H. N. and W. F. Meggers, J. Res. Nat. Bur. Std., 9, 625 (1932).

97. Salpeter, E. W., Ric. Spettroscopiche, Lab. Astrofis. Specola Vaticana, 2, 1 (1952). Original not available; abstracted in Chem. Abstr., 47, 2637 (1953).

98. Sawyer, R. A. Experimental spectroscopy. 3rd ed. New York, New York, Dover Publications, Inc. 1963.

99. Schroll, E. and W. Rockenbauer, Spectrochim. Acta, 11, 338 (1957).

100. Semenova, O. P., Bull. Acad. Sci. USSR, Phys. Ser., 9, 715 (1945).

101. Smolyak, I. I., Bull. Acad. Sci. USSR, Phys. Ser., 19, 199 (1955).

102. Steinhaus, D. W., H. M. Crosswhite, and G. H. Dieke, *J. Opt. Soc. Am.*, **43**, 257 (1953).

103. Stepanov, P. A., E. A. Sergeev, M. V. Belobragina, and M. S. Leshchinskaya, *Bull. Acad. Sci. USSR, Phys. Ser.*, **23**, 1141 (1959).

104. Stone, H., *J. Opt. Soc. Am.*, **44**, 411 (1954).

105. Sugar, J., *J. Opt. Soc. Am.*, **55**, 33 (1965).

106. Sukhodrev, N. K. On spectral excitation in a spark discharge: transactions of the P. N. Lebedev Physics Institute. Vol. 15. New York, New York, Consultants Bureau. 1962.

107. Sventitskii, N. S., *Compt. Rend. Acad. Sci. URSS*, **37**, 205 (1942).

108. Sventitskii, N. S., *J. Tech. Phys.*, **14**, 605 (1944).

109. Takagi, S. and T. Nakamura, *Spectrochim. Acta*, **18**, 389 (1962).

110. Taylor, H. S. and S. Glasstone, eds. A treatise on physical chemistry. 3rd ed. Vol. 1. New York, New York, D. Van Nostrand Co., Inc. 1942.

111. Taylor, W. H. and M. S. W. Webb, *U.S. Atomic Energy Commission Report*, *AERE-R-3875* [United Kingdom Atomic Energy Authority. Research Group. Atomic Energy Research Establishment, Harwell, Berks, England], (1961).

112. Thiers, R. E. and B. L. Vallee, *Spectrochim. Acta*, **11**, 179 (1957).

113. Tveekrem, J. Report for Spectrochemistry Group I, Ames Laboratory. Ames, Iowa, Institute for Atomic Research, U.S. Atomic Energy Commission. 1963.

114. Vilnat, J., A. Abdellatif, and J. Debras-Guedon, *Bull. Soc. Franc. Ceram.*, **61**, 69 (1963).

115. Vilnat, J., J. Debras-Guedon, and A. Abdellatif, *Compt. Rend.*, **257**, 3582 (1963).

116. Vilnat, J. and J. Vignet, *Bull. Soc. Franc. Ceram.*, **63**, 71 (1964).

117. Vorsin, A. N., Bull. Acad. Sci. USSR, Phys. Ser., 19, 138 (1955).

118. Walters, J. P. and H. V. Malmstadt, Anal. Chem., 37, 1477 (1965).

119. Weber, M., Bull. Soc. Chim. France, 4, 805 (1961).

120. Weber, M., Group. Avan. Methodes Anal. Spectrog. Publ., 1960, 247 (1960).

121. Zaidel, A. N., N. I. Kaliteevskii, L. V. Lipis, and M. P. Chaika, U.S. Atomic Energy Commission Report, AEC-tr-5745 [Division of Technical Information Extension, AEC], (1963).

122. Zaidel, A. N., V. K. Prokof'ev, and S. M. Raiskii. Tables of spectrum lines. Berlin, Germany, Veb Verlag Technik. 1955.

123. Zalubas, R., National Bureau of Standards Monograph, 17, (1960).

124. Zhavoronkina, T. K. and O. B. Fal'kova, Fiz. Sb. L'vovsk. Gos. Univ., 4, 549 (1958).

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