SPECTROGRAPHIC DETERMINATION
OF MAJOR CONSTITUENTS
IN COAL AND FLY ASH AND SLAG
BY SOLUTION EXCITATION

DISSERTATION
FOR THE PARTIAL FULLFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTORATE IN CHEMISTRY

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INTRODUCTION

The importance of a rapid and reliable method for determining the elementary composition of coals, ashes and slags is well established.

The analysis of the ash is essential in ash fouling and high temperature ash corrosion investigations, and the viscosity of a liquid coal slag largely depends on its elementary composition. These phenomena constitute major problem areas in the utilization of coal for the production of power today and, it appears, for the long term future.

The metallic constituents of coal can be determined conveniently by analysis of the ash of the coal after combustion. If the ash content of the coal is known, the concentration of the metallic constituents of the coal can be calculated based on the coal ash analysis results.

Classical chemical analytical methods are able to give reliable information about the elementary composition of ashes and slags, but the conventionally used procedures are very time-consuming.

Extensive investigations were carried out recently to develop spectrographic procedures for ash and slag analysis.(1) Further spectrographic investigations(2) showed that the presence of an excess of sodium sulfate minimized the extraneous element effect caused by the sodium sulfate present in the coal ash and an excess of strontium carbonate decreased the extraneous element effect caused by the calcium content of ashes and slags.

This method(2) gave good results, as long as the composition of the samples did not change drastically, and it has been used for a number of years. For example, if the calibration was carried out to cover a concentration range of 20-50% SiO_2, and a sample of 80% SiO_2 was to be analyzed, this change influenced the intensity ratio of the silica/internal standard line pair and the other line pairs as well. In other words, the usefulness of this method covered only a certain concentration range and any drastic deviation from this range caused discrepancies.

A more serious disadvantage was the effect of the chemical combination of the element to be determined. Although this was reduced by the dilution with the buffer developed, it still existed and in some cases it was the cause of significant errors. For example, if the SiO_2 content of a sample was 40% and the calibration was done using SiO_2 (and this 40% concentration was covered by standards), it was very likely that the result obtained fell in the range of about 38-42%. But if the silica in the ash was present as, for example, calcium-aluminum-silicate, the result obtained was in error.

There have been numerous attempts made to solve the matrix effect over the period of the past few years, through use of a solution technique. Malmstadt and Scholz(3) used a Beckman atomizer to spray the solution between horizontally mounted electrodes across which a high voltage spark was impressed. Schalge(4) used a similar technique and used a high voltage spark as a source of excitation. Schalge and Russel(5) developed a spark-in-spray attachment using a Beckman No. 4030 medium bore atomizer. This attachment has been used for the analysis of trace metals in crude oils diluted in toluene. Acid solutions of rocks have also been analyzed for their trace elements. The source of excitation again was a high voltage spark. Muir and Ambrose(6) fused slag samples with a mixture of sodium carbonate and borax and dissolved the fused sample in dilute nitric acid. Using chromium as internal standard, an aliquot of the sample solution was evaporated on a graphite electrode. Uncontrolled AC condensed spark was used as a source of excitation. Dixon (7), analyzing coal ashes, used essentially the same technique for the determination of the major constituents. Work preceding this study proved that both methods lack sensitivity and precision and the work of Angell and Bethell(8) substantiated this conclusion. Meyer and Koch(9) fused the samples with a flux mixture of sodium carbonate-potassium carbonate-borax and dissolved the melt in a hydrochloric acid solution of cobalt nitrate (internal standards). An aliquot was put on a preheated graphite electrode (similar to the techique suggested by Muir and Ambrose) and a high voltage spark discharge was used. This method also was investigated in our laboratory and found to lack the required sensitivity and accuracy.

I too felt that a solution technique held considerable promise, and since the ashes and slags concerned are partially or completely acid insoluble, the fusion technique developed and reported in this report served to overcome this problem. Due to the high silicon content of these ash and slag samples, alkaline fusion had to be used.

An additional problem arises when an alkaline fusion is used to dissolve a sample containing both acidic and basic constituents. The fused mass must be dissolved in acid in order to cause aluminum, iron, etc. to solution; however in an acid medium partially dehydrated silica tends to precipitate. It was evident then, that a method would have to be found to prevent the precipitation of silica.

Since the only absolute way to solve the matrix effect is to produce a common matrix through fusion and subsequent dissolution, and since a high voltage spark could not be used, my investigations employed a unidirectional arc for the source of excitation. An additional great advantage of the arc over the spark is the much higher sensitivity of the arc, thus permitting the reduction of the weight of sample to be analyzed. When arc-excitation of the atoms is used, the spray technique cannot be used any longer because the electrodes overheat. An effective way of cooling the sample electrode (a rotating disc was chosen) was developed and it was found that the best coolant is the solution of sample itself.

Using the rotating disc-type electrode, the solution of sample is transferred onto the disc by a capillary contacting the disc. The disc cannot overheat and the smoothest possible introduction of the sample into the electric arc is achieved.

RESULTS

1. Precision of analyses - In order to evaluate the precision of the method, twelve aliquots of a typical coal ash sample were carried through the entire procedure in the same manner as done in the standardization and the analysis of samples. Table I shows the statistical analysis of the results and illustrates the excellent precision obtained (in the order of ± 1%).

2. Accuracy of analyses - Chemically analyzed coal ash, fly ash and slag samples were analyzed by the new method and a comparison of results is shown in Tables IV and V. It can be seen that very good agreement was obtained with the chemical analyses.

3. Application - Table II summarizes the results obtained by the spectrographic solution excitation method, compared to the chemical analysis of three widely varying types of samples possessing different crystalline constituents.

Table III shows the results obtained on the analysis of Bureau of Standard samples.

From the excellent agreement of the results it appears that the extraneous element effect has been largely reduced or eliminated and that this method may be generally applicable to the analysis of a wide variety of samples. Results indicate independence of crystalline form (Table II) and it appears that the method is indeed of widespread applicability.

4. High voltage AC spark excitation was found to lack the required sensitivity and precision.

5. Self-sustaining AC or DC arcs, due to the extremely high arc temperatures could not be used.

6. Currently available electrodes and electrode systems were not satisfactory for the arc-excitation of the elements from solution.

7. As a result of the above, a new electrode system was designed (Figure 1) which maintains a continuous supply of the sample solution into the excitation zone, permits the use of a continuously ignited arc as a source of excitation and prevents the local and temporary changes of the concentration of the elements near and on the rotating electrode.

8. Due to the higher sensitivity of the arc excitation, the sample weight could be reduced to 15 mg.

9. Only one internal standard line (Ge 2709.63A) was required and it served satisfactorily for fifteen analytical lines of the elements of interest.

10. A technique was developed for the readjusting of the arcing conditions, which prevented the "shifting" of the analytical curves. This phenomenon should always be considered as a major factor in the statistical evaluation of any spectrographic method where continuous ignition is required.

11. A new flux, sodium metaborate ($NaBO_2$) was developed for the fusion of the ash and slag samples. This flux is prepared by reacting equimolecular amounts of sodium tetraborate ($Na_2B_4O_7$) with sodium carbonate (Na_2CO_3) at their melting points:

$$Na_2B_4O_7 + Na_2CO_3 \longrightarrow 4\ NaBO_2 + CO_2$$

The $NaBO_2$ was identified by X-ray diffraction and was found to be a universal flux, being able to fuse all types of coal and fly ashes and slags. The CO_2 formed during the reaction was determined gravimetrically and the amount recovered checked very well to that indicated by the above equation.

12. To keep the silica in solution in an acid medium was one of the most important objectives. It was found that when following the technique described in this report, no dehydration of the silica takes place.

13. It was found that the presence of organic solvents, e.g., isopropyl alcohol, greatly improved the sensitivity and precision of the results.

14. The fluctuation of the arc temperature was effectively reduced by adding an element (sodium) with a low excitation potential to the sample in a large excess.

EQUIPMENT DESCRIPTION

The equipment used in this investigation was a Jarrell-Ash, Wadsworth mounting, 3.4 meter stigmatic grating spectrograph, a National Spectrographic Laboratories Spec-Power source unit, a National Spectrographic Laboratories microphotometer, an Applied Research Laboratories developing machine, an Applied Research Laboratories calculating board, an Applied Research Laboratories film-drying machine, a Jarrell-Ash rotating disc attachment and a Superior Electric Co. Type EMT 4228B Stabiline transistorized, electro-mechanical, 27.5 kva automatic voltage regulator.

The electrode assembly that was designed for this project is shown in diagrammatic form in Figure 1. The electrode assembly is mounted on a Jarrell-Ash Model JA-1930 arc stand.

The graphite tapered mandrel* with the rotating disc** on its tapered end is placed in the center hole of the rotating disc attachment which is placed in the

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*Obtained from the United Carbon Products, Cat. No. UCP-2021

**Obtained from the National Carbon Co., Cat. No: SPK L4275, electrical resistance: 0.00045 ohm/inch, density: 1.90

lower electrode clamp. The 0.180" diameter graphite counter elctrode*** is placed in the upper electrode clamp.

The solution of sample is transferred to the reservoir (Figure 1) and by opening stopcocks Nos. 1 and 2 the solution is allowed to flow through the capillary on the rotating disc. The capillary is in a constant contact with the rotating disc during arcing. The capillary is made in such a manner that the hole faces the rotating disc and allows the solution of sample to pass through it with a flow rate of 12-14 ml/min.

DISCUSSION

Although the dissolutioning of solid samples and the excitation of the atoms from the solution is gaining popularity, there is practically no evidence available in the literature pertaining to a successful attempt to develop a spectrographic procedure for the analysis of materials of a widely varying matrix. Furthermore, very little information is available dealing with the arc exciation of solution samples. This paper describes an accurate, simple and universal procedure for the spectrographic analysis of all types of coal ashes, fly ashes and slags, using a continuously ignited arc as the source of excitation.

A. Effect of Variables

A number of factors were identified as variables greatly influencing the usefulness and reliability of the procedure and these variables are discussed below.

1. Matrix and Extraneous Element Effect

The variation of matrix affects the line intensities. This is called the matrix effect and it is one of the most widely studied factors in spectrochemical analysis.

***Obtained from the National Carbon Co., Cat. No: SPK L3826

One important cause of the matrix effect is selective volatilization resulting mainly from the presence of various anions or radicals. In the method developed, selective volatilization is reduced to a minimum by converting all elments into volatile halides (chloride). The presence of non-metals does not change the arc temperature because of their extremely high ionization potentials. They may, however, influence the line intensities by forming relatively stable molecular complexes with metals in the arc and thereby decrease the number of metal atoms available for excitation. The selective volatilization is minimized when all elements are bonded to the same anion, and in this method it was effectively reduced by converting the elements into volatile halides. Table II shows the results of spectrographic, compared to chemical analysis, of the three common forms of coal ashes and slags possessing widely varying crystalline (or non-crystalline) form. The comparison of the chemical and spectrographic analysis results shows that the change in the crystalline form does not affect the results obtained by the new spectrographic solution-excitation technique.

Another matrix effect arises from the fact that any significant change in the elemental composition of the sample will change the temperature of the arc. A large increase in the concentration of one element may cause a change in the arc temperature, which in turn will change the fraction of atoms excited of the other elements present. This phenomenon is called the extraneous element effect and it is effectively reduced by the addition of a large excess of sodium. Through the addition of such a large amount of sodium, the effective excitation temperature of the arc is kept constant and the temperature changes, which could otherwise be brought about by changes in the sample composition, are masked.

The synthetic standards prepared for the standardization of the procedure all represent extremes in the concentrations of the constituents, but as it is shown in Figure 2, excellent working curves were obtained.

Figure 2 also shows the elimination of the extraneous element effect, which can be seen clearly when comparing the 30% Al_2O_3 points and the 5.6% (10.0% $CaCO_3$) and 2.8% (5.0% $CaCO_3$) CaO points. Thirty percent Al_2O_3 is contained in Standards #2 and #5, the other elements were present in different amounts, and the points corresponding to the 30% Al_2O_3 concentrations were both on the curve. Standards #3 and #6 contain 5.6% CaO and 2.8% CaO is contained in Standards #4 and #7. It can be seen that both the 5.6 and 2.8% CaO points follow the working curves.

The elimination of the extraneous element effect is further illustrated on Table III. The CaO concentration was determined on #102 Silica Brick Bureau of Standard sample, the CaO, Fe_2O_3 and SiO_2 concentration on #104 Burned Magnesite Bureau of Standard sample, the SiO_2, Al_2O_3 and TiO_2 on #97 Flint Clay and the SiO_2, Al_2O_3, TiO_2, CaO and MgO on #98 Plastic Clay Bureau of Standard sample. As it can be seen, very good agreements were obtained.

2. Effect of the Sodium Concentration

(a) Effect of Sodium Concentration on Intensity Ratios.

It was found that increasing sodium concentration decreased the intensity ratios because the intensities of the germanium lines increased strongly with increasing sodium concentration; the intensities of the silicon, aluminum and magnesium lines increased only slightly and the intensities of the calcium and titanium lines decreased with increasing sodium concentration. The intensities of the iron lines did not change appreciably with increasing sodium concentration.

(b) Effect of Sodium Concentration on Calibration.

The sodium concentration of the sample had to be high enough to counteract the effect of any drastic concentration change on the arc temperature and low enough to prevent the supersaturation of the solution and make a convenient fusion possible. Slight deviations from the working curves were obtained when using 2.0 g of flux/15 mg of sample. It was found that when the sodium concentration was increased to use 3.0 g of flux, the points fell on the curves and good calibration was obtained for all the line pairs.

3. Form of the Sodium

The sodium added in excess to control the temperature of the arc is added in the form of the borate-carbonate flux.

Various other chemicals and combinations of them have been used also as sources of sodium prior to taking all the sodium in the form of sodium tetraborate-sodium carbonate. Sodium chloride, sodium phosphate, sodium acetate and sodium citrate were the sources of sodium tested, in the presence of varying amounts of borate-carbonate flux.

It was found that when the sodium was added as the borate-carbonate flux in a sufficiently high concentration, the precision of the results was the highest and the extraneous element effect the lowest.

Equimolecular amounts of anhydrous sodium tetraborate and anhydrous sodium carbonate were brought up to their melting points leading to the formation of sodium metaborate and carbon dioxide:

$$Na_2B_4O_7 + Na_2CO_3 \longrightarrow 4NaBO_2 + CO_2$$

The $NaBO_2$ was identified by X-ray diffraction analysis and was found to be a universal flux being able to fuse all types of coal and fly ashes and slags. The CO_2 was determined gravimetrically and the amount recovered checked very well to that indicated by the above equation.

The segregation of the fused constituents during cooling was prevented by using a slight excess of sodium tetraborate over the stoichiometric amount.

4. Dissolutioning of the Fused Sample

One of the most important objectives of this work was the development of a technique for retaining silicon in solution in an acid medium. It was found that when the fused sample is dissolved according to the technique outlined in the procedure, no dehydration of the silica or formation of colloidal silica takes place.

When the fused samples, particularly the ones containing silicon in high concentrations, are brought in contact with the cold HCl solution and the temperature is raised gradually to boil, partial dehydration of the silica takes place. On the other hand, if the fused sample is transferred to a boiling HCl solution, no dehydration of the silica is observed and apparently a solution of hydrated silica is obtained.

5. Concentration of the HCl Solution

The acid concentration was proved to be another important variable affecting both the dissolutioning of the sodium-silicate and the precision of the results. The concentration range between 1 and 5N was investigated and it was found that low HCl concentrations decreased the precision and high HCl concentrations contributed to the formation of colloidal silica. Complete dissolutioning and highest precision were obtained when 3.0 N HCl solution was used.

6. Effect of the Type of Acid

Two acids were investigated as dissolutioning agents for the fused samples: nitric acid and hydrochloric acid.

Introducing the nitric acid solution and hydrochloric acid solution of the same sample into the arc maintaining identical arcing conditions, and taking the same volume and concentration of both acids, it was found that:

(a) The line intensities of the elements present in the nitric acid solution were several times below those determined when hydrochloric acid was used as the dissolutioning agent. The reason for this is that at arc temperatures, the nitrates more readily decompose to the oxides, and since the volatilities of the oxides are below the volatilities of the chlorides, a smaller number of atoms of each element is available for excitation in a given length of time.

(b) The precision of the results using nitric acid as the dissolutioning agent was far lower than the precision obtained in the presence of hydrochloric acid. This can be explained by assuming that the difference in the boiling points of the oxides, formed as the result of the nitrate decomposition, leads to selective volatilization. Some of the oxides are reduced to the metal or form carbides with the electrode at the arc temperature more readily than others and make the selective volatilization even more pronounced and harder to control. With the use of a hydrochloric acid solution, however, the rapid volatilization of the chlorides will tend to reduce the possibility of forming oxides or carbides.

The conversion of all elements into the volatile chlorides had two important advantages:

1. Due to the higher volatility of the chlorides, smaller amounts of samples are sufficient to produce the same line intensities. Smaller samples contributed sig-

nificantly to the elimination of the extraneous element effect since large changes in the concentration with smaller samples have smaller effect on the arc temperature.

2. It was possible to reduce the selective volatilization to the minimum.

7. Organic Solvent Addition

It was found that under identical test conditions, the sensitivity and precision were greatly improved when organic solvents were added to the solution of sample. Various types of water-soluble organic solvents were considered and isopropyl alcohol was selected for the following reasons: (a) relatively high boiling point, (b) relatively inexpensive, (c) high purity, (d) high solubility in water, (e) low toxicity, and (f) excellent wetting agent. It was found that in the presence of isopropyl alcohol the sensitivity of the procedure approximately tripled. This is also true in flame photometry where its effect is not clearly understood.

8. Sample Electrodes

Before selecting the rotating disc as the most suitable sample-electrode-type for the procedure, unsuccessful experiments were made using the vacuum-cup and porous-cup-type electrodes. The porous-cup and particularly the vacuum-cup-electrodes are fairly well known and successfully used for certain types of liquid samples, but it was found in this laboratory that these two types of electrodes can only be used when the source of excitation is a high voltage spark; self-sustaining or continuously ignited AC or DC arcs cannot be used.

Continuously ignited arcs can be used when a rotating disc is the sample electrode. Self-sustaining arcs, due to the extremely high arc temperatures, cannot be used.

The rotating discs were obtained from the National Carbon Company and are manufactured of two types of graphite:

(a) Low-density grade (d = 1.61 g/ml). This grade is used by several laboratories, mostly for sparking aqueous samples. Its porosity permits this grade to be used for the manufacturing of the porous-cup-type electrodes. The inconsistency and low precision obtained in this laboratory after first using solution-excitation by means of continuously ignited DC arc was explained by this high porosity. Due to the much higher temperature of the ignited arc, as compared to the temperature of the high voltage spark, the sample solution not only evaporates but penetrates the rotating disc as well. The section of the disc with the penetrated and partially or completely evaporated sample solution rotates further and again contacts the fresh solution. This solution dissolves the evaporated and penetrated solids only partially or not at all and enters the arc. It can be seen that the concentration of the sample does not remain constant every time the disc makes a turn. Based on this explanation, the penetration and evaporation of the solution had to be prevented or at least decreased.

(b) High density grade (d = 1.90). Using this grade of rotating discs, the precision of the results showed a distinct improvement, since the penetration of the solution was largely eliminated, although some inconsistency of the results still prevented the final standardization of the procedure. A close and repeated observation of the operating arc showed that the solid residue formed on the surface of the disc may not dissolve completely when again contacting the solution. It can also be assumed that the concentration of the elements of the solution around the rotating disc during arcing may not be the same as that in the rest of the solution due to the continuous dissolutioning of the solid residue formed on the disc after leaving the arc. These considerations made it necessary to develop a different type of sample supply and finally lead to the electrode assembly that was designed to provide a continuous supply of the sample, discharge the aliquot of sample arced and remove all the solid deposits formed on the disc surface before re-entering the arc.

9. The New Electrode System

The new electrode designed for the procedure is shown in diagrammatic form in Figure 1.

The electrode is easy to assemble and easy to handle. The detailed operation is described under "Test Procedure, A. Standardization, 3. Arcing".

The electrode is mounted in a Jarrell-Ash Model JA-1930 arc stand and consists of two main parts:

(a) The rotating disc attachment with a graphite tapered mandrel in its center hole. The rotating disc is placed on the tapered end of the mandrel. The disc attachment is placed in the lower electrode clamp (anode) and the 0.180" diameter graphite counter electrode (cathode) is placed in the upper electrode clamp. The rotating disc attachment is connected with the driving motor, mounted in the arc stand, by means of a non-conducting rod to rotate the disc clockwise with a rate of 10 rpm. An open end combustion boat is placed underneath the rotating disc to discharge the sample.

(b) The sample-supply system consists of the reservoir, 3-way stopcocks, squeeze-bulb, connecting glass tubing, glass joints to disassemble the system and the capillary. In order to effect efficient cooling and rinsing of the rotating disc, the capillary is in continuous contact with the disc and is prepared in such manner that the hole faces the rotating disc and allows the solution of sample to pass through it with a flowrate of 12-14 ml/min.

This new electrode provides a continuous supply of the sample, introduces a representative aliquot of the sample in the arc and prevents any fluctuations in the concentration of the elements by continuously removing the evaporated residue.

Table I shows the precision of results obtained by the procedure using the new electrode and maintaining the standardized arcing conditions previously described in detail.

The data used for the precision study and statistical evaluation were obtained as follows:

An actual coal ash sample was taken and twelve 15.0 mg aliquots of it were passed through the entire procedure. Two exposures were made with each solution, as it was done with the standardization and the analysis of samples, and the average of the two intensity ratios obtained $\frac{\log I_{\text{element, wavelength}}}{\log I_{\text{Ge, 2709.63 Å}}}$ was taken for the calculations.

10. Flow Rate

Holding all the variables constant, the flow rate was varied between 7-15 ml/min. It was found that while no marked differences in the intensity ratios were obtained, the precision of the results increased with increasing flowrate. A flowrate of 12-14 ml/min was found to give the highest precision and the standardization of the procedure, the precision study and the analysis of the samples all were performed using this flowrate.

11. Effect of Voltage Fluctuations

A spark primary voltage of 120V was maintained with an auxiliary gap of 4.0 ± 0.1 mm to produce 2 breaks per half cycle.

Periodic fluctuations were observed in the spark primary voltage as a result of the ± 8 V variation in the line voltage (216-232 V), causing significant decrease in precision of the calcium-germanium line-pairs (both the 3158.87 and 3179.33 Å Ca-lines are spark lines) and affecting the lines of the other elements as well.

To increase the precision of the calcium results and the results of the other elements as well, a Superior Electric Company transistorized, electro-mechanical, 27.5 KVA automatic voltage regulator was installed.

The voltage regulator decreased the fluctuation of the line voltage to ± 0.5 V. This small fluctuation did not seem to have any marked effect on the intensity ratios or on the precision of the results. An output voltage (from the voltage regulator to the source unit) of 225 V was maintained.

12. Effect of the Variation of the Amperage

The effect of the variation of the amperage on the intensity ratios of the line pairs and precision was studied between the range of 5-12 A. An amperage of less than 6 did not provide a sufficient degree of excitation and an amperage of over 10 decreased the precision of the results. Figures 3-4 show the effect of the variation of the amperage on the intensity ratios of the element/Ge line-pairs.

Figure 3 shows no significant variation in the intensity ratios of the Al/Ge, the Si 2506/Ge and the Si 2519/Ge line-pairs, while the intensity ratios of the Si 2435/Ge line-pair give flat maximum curves. The intensity ratios of the Fe/Ge line-pairs show a decrease of the intensity ratios with increasing amperage.

Figure 4 shows that the intensity ratios of the two Ca/Ge line-pairs give flat maximum curves, the intensity ratios of the Mg/Ge line-pairs increase with increasing amperage and the Ti/Ge intensity ratios give sharp maximum curves, showing the highest sensitivity of the line-pairs to the variation of the amperage. The source-unit, however, maintains a current stable enough at any of the five values not to cause any "shifting" in the Ti-working curves using any of the currents between 6-10A.

B. Analysis of Samples

Tables IV and V show the spectrographic analysis results obtained on actual coal ash, slag and fly ash samples. Comparing these results with the classical chemical analysis results, it can be seen that very good agreements are obtained on all of these different types of samples.

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TABLE I

STATISTICAL ANALYSIS OF THE RESULTS

Constituent	Wave length of spectrum line used (A)	Concentration (percent)	$\bar{X}$ (percent)	Standard deviation ± % b. wt. of the constituent
SiO_2	2435.16	46.0, 46.0, 46,0, 45.5, 46.5, 46.0 46.0, 45.5, 46.0, 46.0, 46.5, 46.0	46.0	± 0.3
Al_2O_3	2660.39	24.3, 24.5, 24.7, 24.7, 24.3, 24.5 24.5, 24.3, 24.3, 24.5, 24.3, 24.5	24.4	± 0.16
Fe_2O_3	3008.14	8.4, 8.6, 8.4, 8.3, 8.5, 8.4 8.4, 8.6, 8.6, 8.4, 8.6, 8.3	8.5	± 0.12
TiO_2	3236.57	1.15, 1.12, 1.20, 1.12, 1.08, 1.17 1.15, 1.20, 1.12, 1.18, 1.18, 1.17	1.15	± 0.03
CaO	3158.87	5.10, 5.18, 5.23, 5.23, 5.30, 5.12 5.23, 5.30, 5.00, 5.23, 5.12, 5.02	5.17	± 0.10
MgO	2779.83	2.20, 2.24, 2.22, 2.33, 2.24, 2.22 2.22, 2.22, 2.24, 2.21, 2.25, 2.22	2.23	± 0.03

TABLE II

ANALYSIS OF THE THREE MAJOR TYPES OF SAMPLES

	B-16664 (Coal Ash)		K-19319 (Fly Ash)		K-19404 (Slag)	
X-Ray Diffraction Analysis						
Major	α Quartz		α Quartz		FeS	
Minor	$CaSO_4$, Fe_2O_3		Fe_3O_4 (Spinel)		α Fe	
Remarks	Strong pattern		Very strong pattern		Poor pattern, mostly non-crystalline	
Elemental Analysis (As Oxides)						
	Chem.	Spec.	Chem.	Spec.	Chem.	Spec.
SiO_2	40.1	42.0	53.9	52.7	30.9	29.5
Al_2O_3	24.4	25.0	17.0	17.5	16.1	15.4
Fe_2O_3	12.3	12.0	16.2	15.7	24.3	27.5
TiO_2	1.3	1.5	0.5	0.7	0.5	0.6
CaO	9.2	8.3	0.7	1.1	0.7	0.7
MgO	2.5	2.6	7.4	7.3	0.4	0.5
C					15.9	

TABLE III

ANALYSIS OF BUREAU OF STANDARD SAMPLES

	#102 Silica Brick		#104 Burned Magnesite		#97 Flint Clay		#98 Plastic Clay	
	Std. Comp.	Spec.	Std. Comp.	Spec.	Std. Comp.	Spec.	Std. Comp.	Spec.
SiO_2	93.94	92.*	2.54	2.8	42.87	41.2	59.11	57.5
Al_2O_3					38.77	38.0	25.54	25.5
Fe_2O_3			7.07	6.7	0.98		2.05	
TiO_2					2.38	2.6	1.43	1.4
CaO	2.29	2.1	3.35	3.4			0.21	0.2
MgO			85.67				0.72	0.6

*Obtained by extrapolating the $\frac{2435.16 \text{ Å Si}}{2709.63 \text{ Å Ge}}$ curve

TABLE IV

COMPARISON OF COAL ASH ANALYSIS WITH CHEMICAL ANALYSIS

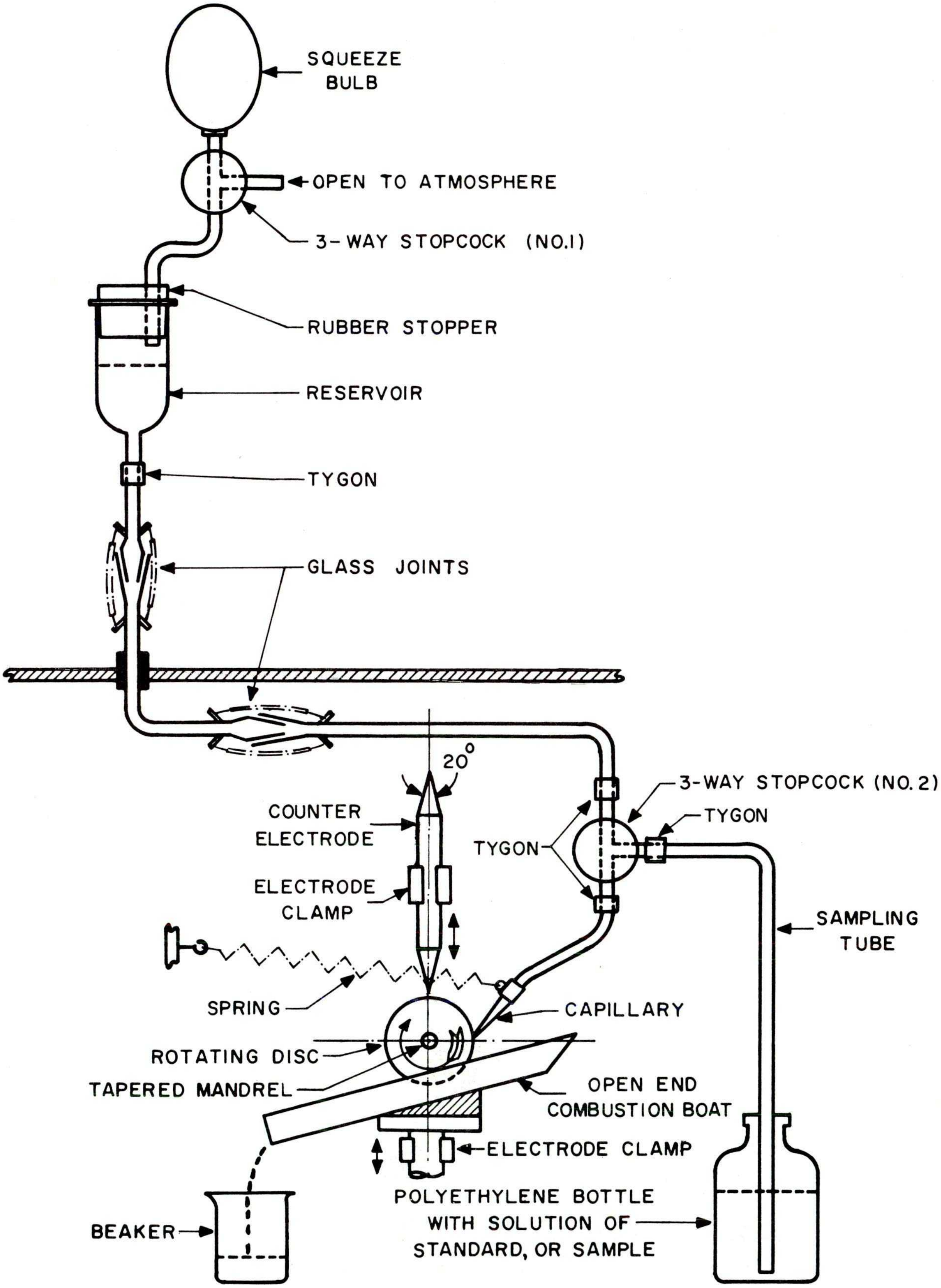
	B-16664		B-15985		B-16286		B-16316	
	Chem.	Spec.	Chem.	Spec.	Chem.	Spec.	Chem.	Spec.
SiO_2	40.1%	42.0%	45.0%	46.8%	48.7%	51.0%	47.8%	47.0%
Al_2O_3	24.4	25.0	29.2	29.3	29.1	28.0	23.5	24.5
Fe_2O_3	12.3	12.0	14.7	16.3	5.1	4.6	9.9	8.8
TiO_2	1.3	1.5	0.9	1.4	1.0	1.0	1.2	1.2
CaO	9.2	8.3	3.0	3.1	5.1	5.1	5.6	5.1
MgO	2.5	2.6	0.9	0.9	2.6	2.0	2.3	2.2

	B-16706		B-21106		K-12665		M-17080	
	Chem.	Spec.	Chem.	Spec.	Chem.	Spec.	Chem.	Spec.
SiO_2	52.2%	53.2%	21.8%	19.0%	37.4%	34.7%	42.8%	42.5%
Al_2O_3	25.3	26.0	9.1	8.6	19.4	19.0	22.4	23.0
Fe_2O_3	15.0	15.1	23.1	23.5	20.5	20.5	25.2	27.6
TiO_2	0.8	1.2	0.5	0.4	1.2	1.5	0.7	1.0
CaO	2.6	2.4	18.4		3.5	3.3	2.6	2.8
MgO	1.1	0.9	7.2	5.5	2.1	1.3	1.5	1.1

TABLE V

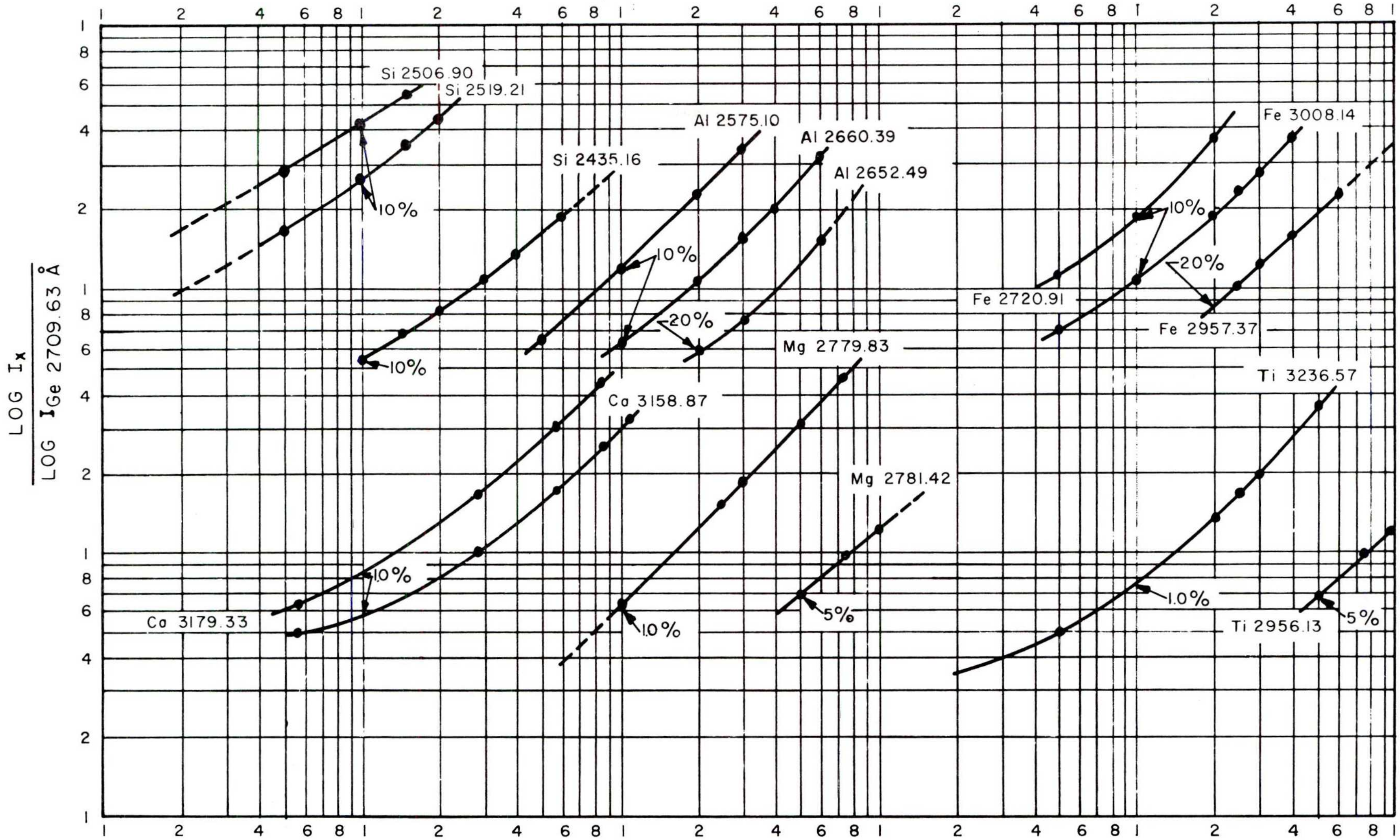
COMPARISON OF SLAG AND FLY ASH ANALYSIS WITH CHEMICAL ANALYSIS

	Slag						Fly Ash					
	K-19352		K-19404		K-19511		K-19319		K-19618		K-19620	
	Chem.	Spec.	Chem.	Spec.	Chem.	Spec.	Chem.	Spec.	Chem.	Spec.	Chem.	Spec.
SiO_2	37.3%	36.0%	30.9%	29.5%	54.0%	54.0%	53.9%	52.7%	46.0%	45.7%	44.8%	44.0%
Al_2O_3	15.5	19.5	16.1	15.4	28.1	26.5	17.0	17.5	19.8	19.0	19.3	18.5
Fe_2O_3	42.0	38.0	24.3	27.5	12.6	11.5	16.2	15.7	23.0	21.5	22.7	23.7
TiO_2	0.7	0.8	0.5	0.6	0.8	1.2	0.5	0.7	0.8	0.8	0.7	0.8
CaO	0.8	0.9	0.7	0.7	1.4	1.2	0.7	1.1	5.1	5.2	6.0	6.2
MgO	0.4	0.6	0.4	0.5	0.7	1.0	7.4	7.3	1.1	0.9	0.7	0.9
C	0.8		15.9		1.5							



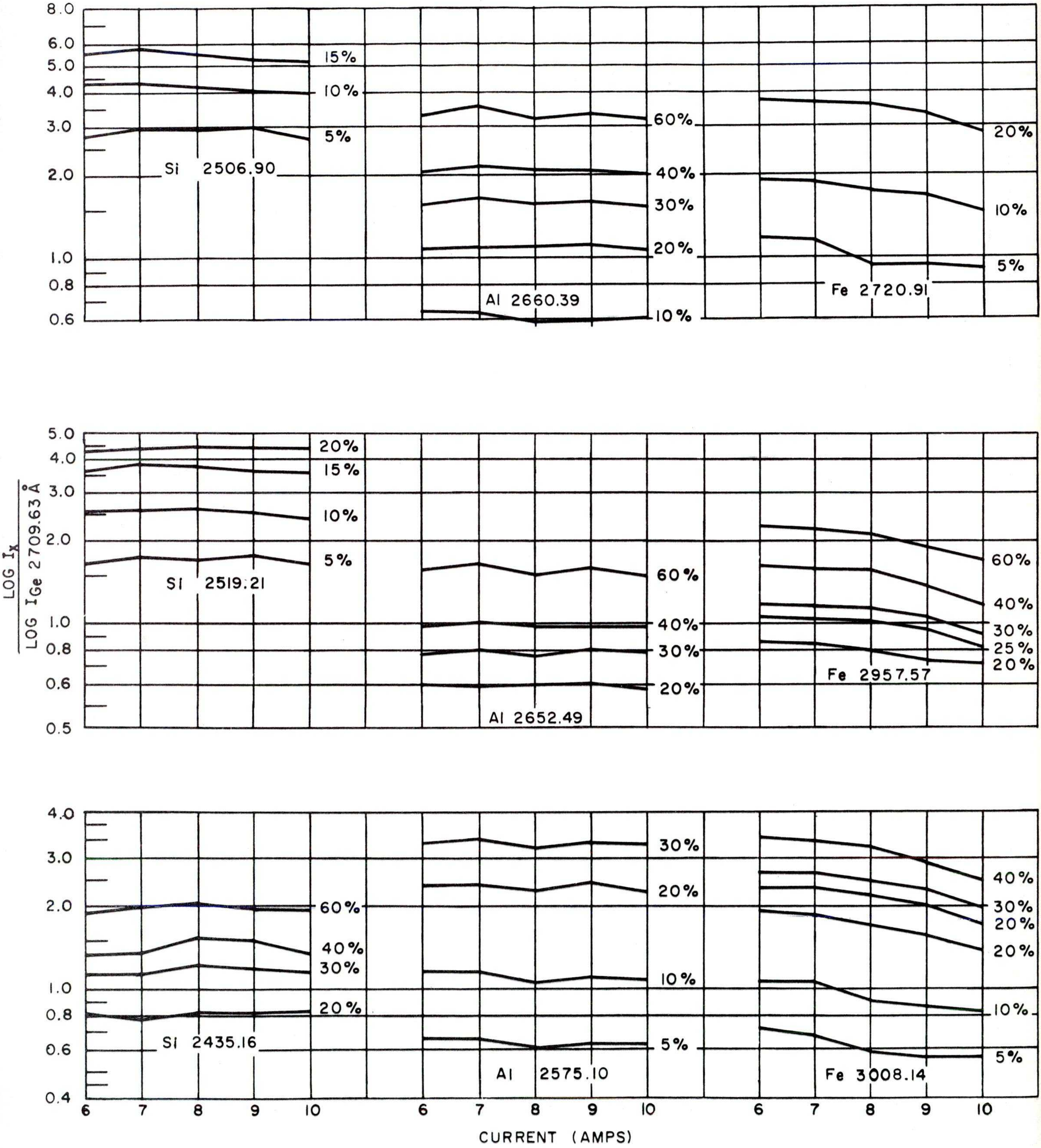
THE MODIFIED ROTATING DISC ELECTRODE SYSTEM

FIGURE 1



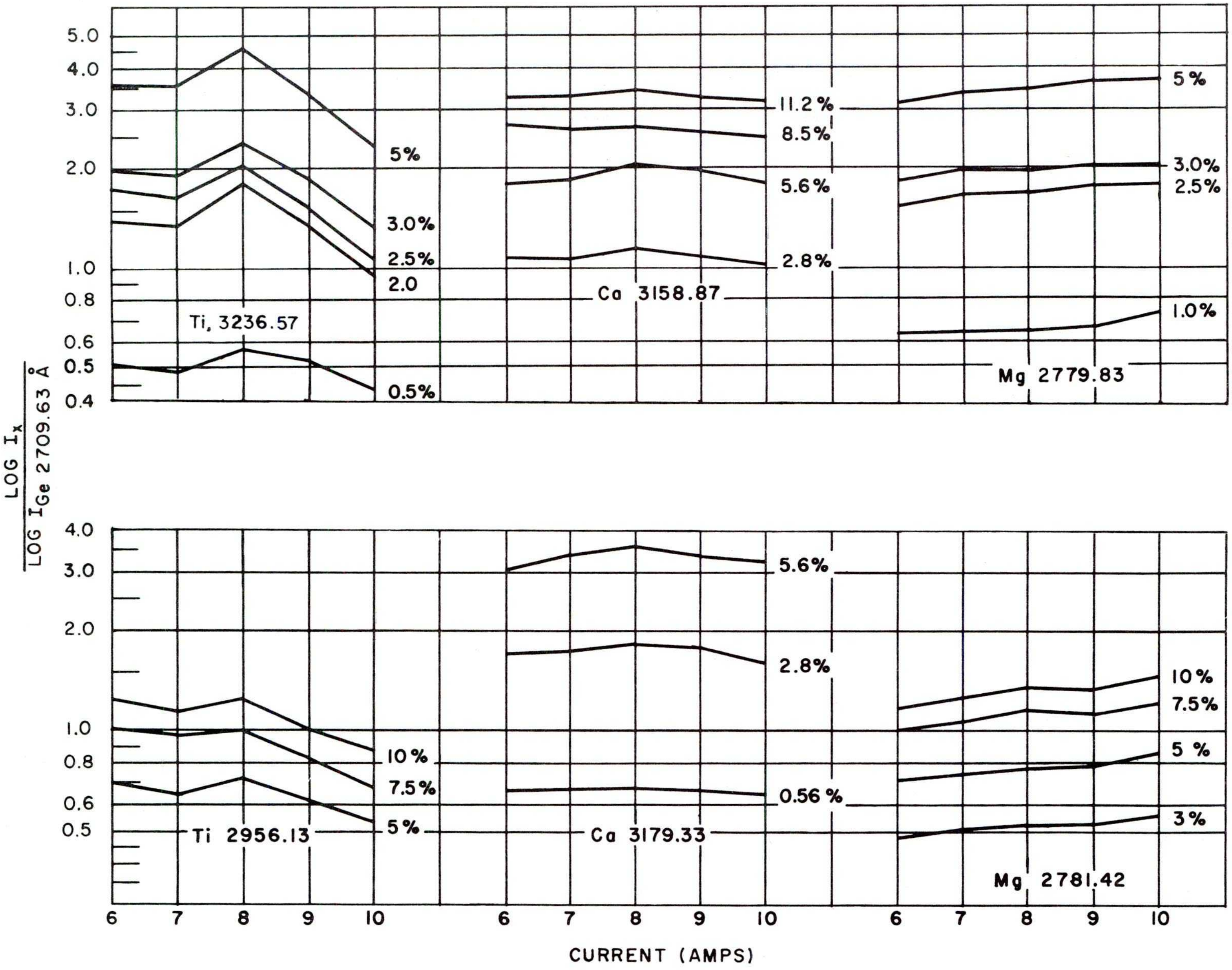
ANALYTICAL CURVES FOR COAL ASH, FLY ASH, AND SLAG. (CONCENTRATION IN % AS THE OXIDE)

FIGURE 2



VARIATION OF INTENSITY RATIOS WITH CURRENT
(CONCENTRATION IN % AS THE OXIDE)

FIGURE 3



VARIATION OF INTENSITY RATIOS WITH CURRENT
(CONCENTRATION IN % AS THE OXIDE)

FIGURE 4

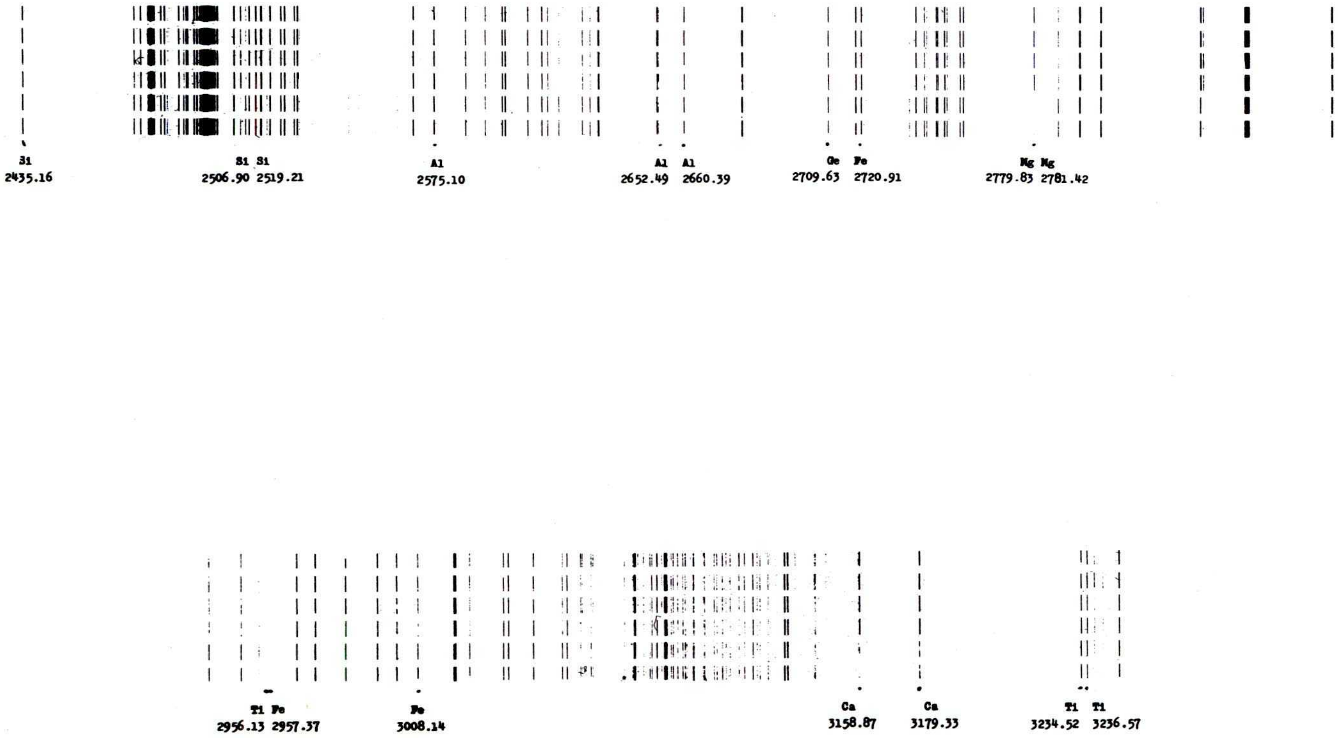


FIG. 5

THE SPECTRA OF ASH SAMPLES

APPENDIX

SPECTROGRAPHIC DETERMINATION OF MAJOR CONSTITUENTS IN COAL ASH, FLY ASH AND SLAG BY SOLUTION EXCITATION

I. Brief of Method

The sample is fused with $NaBO_2$, dissolved in dilute HCl and the solution of sample is introduced into the continuously ignited, unidirectional arc.

II. Equipment and Reagents

A. Excitation of Standards and Samples

1. Jarrell-Ash, Wadsworth mounting, 3.4 meter stigmatic grating spectrograph.
2. National Spectrographic Laboratories Spec-Power Source Unit.
3. National Spectrographic Laboratories microphotometer.
4. Applied Research Laboratories developing machine.
5. Applied Research Laboratories calculating board.
6. Applied Research Laboratories film-drying machine.
7. Jarrell-Ash rotating disc attachment.
8. Superior Electric Co. Type EMT 4228 Stabiline transistorized, electromechanical, 27.5 kva automatic voltage regulator.
9. Jarrell-Ash Model JA-1930 arc stand.
10. Electrode-assembly (Figure 2).
11. Tapered mandrel (United Carbon Products, Cat. No. UCP-2021).
12. Rotating disc (National Carbon Co., Cat. No. SPK L4275, electrical resistance: 0.00045 ohm/inch, density: 1.90).
13. 0.180" dia. graphite counter electrode (National Carbon Co., Cat. No. SPK L3826).
14. Spectrum Analysis No. 1 film (Eastman Kodak Co., Cat. No. SA-421-1).

B. Preparation of Standards and Samples

1. Platinum Crucible, 8 cc, with reinforced top and bottom (J. Bishop & Co.).
2. Hot plate, electrical.
3. Gas burner.
4. Burette stand.
5. Analytical balance.
6. Mixer mill (Spex Industries).
7. Mixing vials (Spex Industries, Cat. No. 6135).
8. Plexiglass ball pestles (Spex Industries, Cat. No. 3112).
9. Polyethylene bottles, 1 l, 500 and 250 ml.
10. Pharmaceutical graduate, 30 ml.
11. Graduate cylinder, 250 ml.
12. Watch glass.
13. Stirring rod.

14. Beaker, 100 ml.
15. Pipettes, 5 ml, 20 ml, and 25 ml.
16. Volumetric flasks, 100 ml, 500 ml, and 1 l.

C. Reagents

1. Distilled water
2. Hydrochloric acid (HCl), reagent grade; 37-38% b. wt; sp.gr. 1.19.
3. Acetic acid (CH_3COOH), reagent grade; 99.7% b. wt.
4. 2 - Propanol (isopropyl alcohol; $CH_3CHOHCH_3$), reagent grade, b.p. 82.3°C (J. T. Baker Chemical Co.).
5. Sodium carbonate anhydrous (Na_2CO_3), reagent grade (Mallinckrodt Chemical Works).
6. Sodium tetraborate anhydrous ($Na_2B_4O_7$), reagent grade (Mallinckrodt Chemical Works).
7. Silicon dioxide (SiO_2), "Specpure" (Johnson, Matthey & Co., Ltd.).
8. Aluminum trioxide (Al_2O_3), "Specpure" (Johnson, Matthey & Co., Ltd.).
9. Ferric trioxide (Fe_2O_3), "Specpure" (Johnson, Matthey & Co., Ltd.).
10. Titanium dioxide (TiO_2), "Specpure" (Johnson, Matthey & Co., Ltd.).
11. Calcium carbonate ($CaCO_3$), "Specpure" (Johnson, Matthey & Co., Ltd.).
12. Magnesium oxide (MgO), "Specpure" (Johnson, Matthey & Co., Ltd.).
13. Germanium dioxide (GeO_2), "Specpure" (Johnson, Matthey & Co., Ltd.).
14. Sodium metaborate flux: Transfer 14.00 g of anhydrous sodium tetraborate and 6.00 g of anhydrous sodium carbonate to a mixing vial. Add 4-5 plexiglass ball pestles, cover the vial and place it in a mixer mill and mix for 30 minutes. Remove from the mill and store in a desiccator. (1.0 g of the sodium-metaborate flux contains 0.70 g of anhydrous sodium tetraborate and 0.30 g of anhydrous sodium carbonate.)

D. Solutions

1. Hydrochloric acid, 3.0N. Transfer 500 ml of distilled water to a 1 liter volumetric flask. Add during continuous stirring 240 ml of concentrated hydrochloric acid (37-38% b. wt., sp.gr. 1.19) and cool in water bath to room temperature. Dilute to mark with distilled water, mix well and store in a polyethylene bottle.

2. Germanium internal standard solution. Transfer 3.0 g of the borate-carbonate flux to an 8 cc platinum crucible and add 60.0 mg of "Specpure" germanium dioxide to it. Mix thoroughly with a small nichrome spatula and cover the crucible. Bring the content to melt carefully and gradually in 5 minutes over a gas burner. (Suggested technique: place the crucible on a triangle and move it gradually into the flame.) Mix the crucible and its content by the end of the triangle and keep it in the flame for 5 more minutes. Remove the crucible from the flame again by the triangle and let it cool on air for 10 minutes. Transfer the cover and crucible with the cold salts to a 100 ml beaker containing 25.0 ml of boiling 3.0N HCl and cover the beaker immediately with a watch-glass (to save time, the 3.0N HCl solution can be brought to boil while the flux is being cooled). Dissolve the solids completely and keep the solution at boiling for 2-3 more minutes. (Total time

of dissolutioning plus boiling should take 5 minutes. The solids are completely dissolved in the boiling HCl solution in about 2-3 minutes.) Remove the beaker with the solution from the hot plate and add 30 ml of distilled water from a pharmaceutical graduate to the solution to prevent supersaturation during cooling and stir. Place the beaker with the dissolved salts into a cold water bath and let it cool for 5 minutes. Rinse the watch glass, stirring rod, the crucible and the cover with distilled water and transfer the germanium solution to a 500 ml volumetric flask containing 300 ml distilled water. Rinse the beaker, transfer the rinsings to the volumetric and dilute to mark with distilled water. Mix and transfer the solution to a 500 ml polyethylene bottle for storage. 5.0 ml aliquots of this solution are taken for the preparation of the solutions of samples and/or standards (Note).

III. Synthetic Standards

Make up a set of synthetic standards by mixing thoroughly the following amounts of "Specpure" chemicals in a mortar (a total of 1.0 g of each standard is recommended to be mixed):

	#1 %	#2 %	#3 %	#4 %	#5 %	#6 %	#7 %
SiO_2	10.0	20.0	30.0	40.0	60.0	15.0	5.0
Al_2O_3	40.0	30.0	20.0	10.0	30.0	5.0	60.0
Fe_2O_3	10.0	20.0	30.0	40.0	5.0	60.0	25.0
$CaCO_3$	20.0	15.0	10.0	5.0	1.0	10.0	5.0
MgO	10.0	7.5	5.0	2.5	1.0	9.5	3.0
TiO_2	10.0	7.5	5.0	2.5	3.0	0.5	2.0

IV. Test Procedure

A. Standardization

1. Preparation of Standards

a. Transfer 3.0 g of the borate-carbonate flux to an 8 cc dry and clean platinum crucible.

b. Transfer 15.0 mg of standard #1 to the crucible and mix it thoroughly with the flux.

Note 1: The platinum crucible is stored in 1:1 HCl solution. Important: The crucible used for the fusion of the GeO_2 is to be used only for that purpose. Do not fuse samples or synthetic standards in this crucible.

c. Place the crucible on a platinum triangle and bring the mixture to the melting point by gradually introducing the crucible into a reducing gas flame. The process of melting the mixture should take 5 minutes.

d. Mix the content of the crucible by the triangle for 15-20 seconds and keep the fused salts fused for 5 more minutes.

e. Remove the crucible from the flame and let it cool to room temperature in 10 minutes.

f. While the fused standard is being cooled, transfer 25.0 ml of 3.0N HCl solution to a 100 ml beaker, place a stirring rod in the beaker, cover with a watch-glass and heat the solution to a smooth boil on an electric hot plate.

g. Transfer the cover and the crucible with the fused salts to the boiling HCl solution and cover the beaker immediately. Keep the solution boiling until the salts are completely dissolved and boil for an additional 2-3 minutes. (Total time of dissolutioning plus boiling should take 5 minutes. The solids are completely dissolved in the boiling HCl solution in about 2-3 minutes.)

h. Remove the beaker from the hot plate, add 30 ml of distilled water from a pharmaceutical graduate to prevent supersaturation during cooling, stir, place the beaker with the dissolved salts into a cold water bath and let it cool for 5 minutes.

i. Remove the solution from the cold water bath, rinse the watch glass, platinum cover, crucible and stirring rod with distilled water and transfer the solution to a 100 ml volumetric flask. Rinse the beaker with distilled water. (Care must be exercised not to overdilute the sample while rinsing the crucible, cover, etc.)

j. While the solution is being mixed, add 5.0 ml of the germanium internal standard solution and 20.0 ml of isopropyl alcohol to the solution. Dilute to mark with distilled water, mix, and transfer to a 250 ml polyethylene bottle. This solution is ready to be transferred to the reservoir of the electrode assembly.

Repeat steps a through j with standards #2, #3, #4, #5, #6 and #7.

2. Arcing Conditions

Source: Uniarc
Spark power: Position #1
Spark primary variac: 4.8
Spark primary voltage: 120v
Arc power: Position #1

UV source: On
Mask: Down
Intensity filter: Off
Wave length, = 2900 A
Order: 2nd
Sector: Off, height of spectrum-lines: 1 step, set by means of the step-sector and Hartman diaphragm.
Input voltage: 225 V (Stabilized, output on the Stabiline Voltage Regulator)
Slit width: 30 u
Capacitance, C_s = 0.0025 u F
Inductance, L_s = 300 u H
Resistance, R_s = 0
Breaks per half cycle: 2 (see Note)
Auxiliary gap, G_x = 4.0 ± 0.1 mm
Analytical gap, G_A = 2.0 mm
Current intensity: I = 7.2 A
Pre-spark, t_{ps} = 20 sec
Exposure, t_{exp} = 30 sec
Intensity switch: High
Programmer: 1, timer: on
Counter-electrode (cathode): National Carbon Type SPK-L3826, 0.180" dia., pointed
Sample-electrode (anode): National Carbon Type SPK-L4275, rotating disc

3. Arcing

   a. Place about 150 ml of distilled water in a beaker and pump it into the reservoir through the sampling tube. Then open stopcock No. 1 to the atmosphere and rinse the capillary by turning stopcock No. 2.
   b. Drain the rinsing water and remove excess water by means of the squeeze bulb. Pump about 10-15 times and wipe the sampling tube dry.
   c. Place the dry sampling tube in the polyethylene bottle containing the solution of Std. #1 and pump about 15-20 ml of it into the reservoir. Rinse the capillary with the solution, remove the sample bottle and drain the solution. Remove the excess of the rinsing solution-aliquot by means of the squeeze bulb. Pump again about 10-15 times.
   d. By means of the squeeze bulb, transfer the solution of standard to the reservoir.
   e. Place the pointed graphite counter-electrode in the upper electrode clamp and the graphite tapered mandrel with the rotating disc on its tapered end in the rotating disc attachment, then place the attachment into the lower electrode clamp. Center the disc and the counter electrode and connect the disc

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Note: Set the 120 V spark primary voltage with the spark primary voltage-adjusting variac and the two full breaks with the auxiliary gap. The adjustment of the breaks is controlled by the oscilloscope.

attachment with the driving motor by means of a non-conducting rod (bakelite, for example).

f. Turn the capillary around the tygon connecting piece to face the rotating disc and connect it with the spring to maintain a continuous contact with the disc during arcing.

g. With stopcock No. 1 open to the atmosphere, start the flow of solution through the capillary by opening stopcock No. 2. Turn on the rotating disc attachment driving motor and keep rinsing the rotating disc with the solution of standard for 30 sec. During this 30 seconds make sure again that the capillary is perfectly centered on the disc.

h. Arc the solution according to the conditions outlined above. Make two exposures (change rotating disc and counter elctrode after each exposure. Using one step high spectrum lines, 6 exposures can be made on one strip of film), and use the arithmetical average of the intensity ratios obtained for the further steps of standardization.

i. Drain the remaining portion of the solution and remove the excess of it by means of the squeeze bulb. Pump 10-15 times, and follow the steps from a through h taking standard #2, #3, #4, #5, #6 and #7.

4. Film Processing

a. Place the film in the soution of the Eastman D-19 developer and develop for 2-1/2 minutes.

b. Transfer the film to a stop-bath (dil. acetic acid solution) for 15 sec.

c. Transfer the film to the acid fix solution for 2-1/2 minutes.

d. Rinse the film well, wipe off the excess water and put the film in the dryer for 2-1/2 minutes.

5. Determination of the Transmittancies of Spectrum Lines and Calculation of the Intensity Ratios

a. Mark the spectrum lines of the elements and the internal standard by means of a previously prepared master-film.

b. Determine the transmittancies of the lines of the elements and of the internal standard by means of the microphotometer.

c. Calculate the intensity ratios of the element lines-to-internal standard line using a gamma curve covering the second order of the 3000 A wave length region. (Note)

d. Plot the intensity ratios vs the concentrations on a 2 x 2 cycle logarithmic paper.

Note: The 3175.45 and 3205.40 Å Fe lines were used to calibrate the spectroscopic film and the ratio has been determined photoelectrically as $\frac{\text{Fe } 3205.40}{\text{Fe } 3175.45} = 1.69$

6. Line Pairs

All line pairs were determined using the 2709.63 Å germanium internal standard line. The following table shows the line pairs and the concentration range for each:

Element Ge	Line Pair Å	Concentration Range (% b. wt.)	Intensity and Character(1)	Excitation Potential of Element Line (eV)
$\frac{\text{Si}}{\text{Ge}}$	$\frac{2435.16}{2709.63}$	20-60	26	5.87
$\frac{\text{Si}}{\text{Ge}}$	$\frac{2519.21}{2709.63}$	2-10	120	4.93
$\frac{\text{Si}}{\text{Ge}}$	$\frac{2506.90}{2709.63}$	below 2 up to 5	170	4.95
$\frac{\text{Al}}{\text{Ge}}$	$\frac{2652.49}{2709.63}$	30-60	15	4.66
$\frac{\text{Al}}{\text{Ge}}$	$\frac{2660.39}{2709.63}$	10-40	20	4.66
$\frac{\text{Al}}{\text{Ge}}$	$\frac{2575.10}{2709.63}$	5-20	48	4.81
$\frac{\text{Fe}}{\text{Ge}}$	$\frac{2957.37}{2709.63}$	20-60	32	4.30
$\frac{\text{Fe}}{\text{Ge}}$	$\frac{3008.14}{2709.63}$	5-30	90	4.23
$\frac{\text{Fe}}{\text{Ge}}$	$\frac{2720.91}{2709.63}$	(1)-10	120	4.61
$\frac{\text{Ca}}{\text{Ge}}$	$\frac{3158.87}{2709.63}$	1-10	20	7.05
$\frac{\text{Ca}}{\text{Ge}}$	$\frac{3179.33}{2709.63}$	0.5-5	50	7.09
$\frac{\text{Mg}}{\text{Ge}}$	$\frac{2781.42}{2709.63}$	3-10	32	7.17
$\frac{\text{Mg}}{\text{Ge}}$	$\frac{2779.83}{2709.63}$	1-5	90	
$\frac{\text{Ti}}{\text{Ge}}$	$\frac{2956.13}{2709.63}$	3-10	150	4.24
$\frac{\text{Ti}}{\text{Ge}}$	$\frac{3236.57}{2709.63}$	0.5-3	440	3.86

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(1) Table of Spectral Line Intensities NBS Monograph 32

B. Sample Analysis

1. Preparation of Samples

Follow the steps described under IV A, Standardization; 1 Preparation of Standards, steps a through j.

2. Arcing Conditions

Identical conditions are to be maintained to those described under IV A, Standardization; 2 Arcing Conditions.

3. Arcing

Follow the steps described under IV A, Standardization; 3 Arcing.

4. Film Processing

Identical to that described under IV A, Standardization; 4 Film Processing.

5. Determination of the Transmittancies of Spectrum-Lines and Calculation of the Intensity Ratios.

Follow the steps described under IV A, Standardization; 5 Determination of the Transmittancies of Spectrum Lines and Calculation of the Intensity Ratios, steps a through c.

6. Determination of the Concentrations of the Elements of the Sample.

The respective element line-to-internal standard intensity ratio values obtained are converted to concentration - % by weight - values by menas of the working curves obtained following the steps of A, Standardization.

B. Sample Analysis

1. Preparation of Samples

Follow the steps described under IV A, Standardization; 1 Preparation of Standards, steps a through j.

2. Arcing Conditions

Identical conditions are to be maintained to those described under IV A, Standardization; 2 Arcing Conditions.

3. Arcing

Follow the steps described under IV A, Standardization; 3 Arcing.

4. Film Processing

Identical to that described under IV A, Standardization; 4 Film Processing.

5. Determination of the Transmittancies of Spectrum-Lines and Calculation of the Intensity Ratios.

Follow the steps described under IV A, Standardization; 5 Determination of the Transmittancies of Spectrum Lines and Calculation of the Intensity Ratios, steps a through c.

6. Determination of the Concentrations of the Elements of the Sample.

The respective element line-to-internal standard intensity ratio values obtained are converted to concentration - % by weight - values by menas of the working curves obtained following the steps of A, Standardization.