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Development of Methods for the Determination of Major and Minor Elements and Hydrocarbon Residues in Solid Combustion Products

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DEVELOPMENT OF METHODS FOR THE DETERMINATION OF MAJOR AND MINOR ELEMENTS AND HYDROCARBON RESIDUES IN SOLID COMBUSTION PRODUCTS

A Thesis

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Master of Science

by

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DEVELOPMENT OF METHODS FOR THE DETERMINATION OF MAJOR AND MINOR ELEMENTS AND HYDROCARBON RESIDUES IN SOLID COMBUSTION PRODUCTS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

DEVELOPMENT OF METHODS FOR THE DETERMINATION OF MAJOR AND MINOR ELEMENTS AND HYDROCARBON RESIDUES IN SOLID COMBUSTION PRODUCTS

Xiaoliu (Charley) Chi   May 1997   58 pages

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ABSTRACT

Methods for the determination of inorganic constituents in coal fly ash by glow discharge spectrometry (GDS) and for the extraction of the organic compounds from coal and ash by supercritical fluid extraction (SFE) at temperatures below 150°C are reviewed. The inorganic elements studied included Al, Ca, C, Cu, Fe, Mg, Mn, P, S, Si and Ti. The organic compounds were measured by weight loss of the sample. The goal of this research was to find easier and faster ways to measure the concentration of inorganic elements in coal ash and to measure extractability of the coal itself, to make coal conversion and utilization more efficient and convenient.

The results of this research indicated that for inorganic element determination, graphite can be used as the host material to make the coal ash pellets. When 90% graphite and 10% ash were mixed together and compressed under 20 tons of pressure, the pellets had suitable conductivity and mechanical strength, and the calibration curves for most of the elements were linear, especially for Al and Si. Copper was also used as the host material. In copper

ix

pellets the intensities of all elements were much larger than those in graphite, indicating that copper is more promising for pellet preparation.

For supercritical fluid extraction, temperature is an important factor for extraction efficiency. The pressure and kinds of modifiers used were also important for extraction. The weight loss by supercritical fluid extraction of coal was much smaller than by soxhlet extraction, indicating that it is difficult to extract organic compounds from coal by SFE at temperatures below 150°C.

I. INTRODUCTION

The ultimate need to replace liquid and gaseous fuels now derived from petroleum and natural gas resources with synthetic fuels from coal is generally recognized. Although technological bases already exist for utilizing coal directly in combustion and for converting it to liquid and gaseous fuels, considerable improvements in these technologies (such as greater overall thermal efficiency, hydrogen utilization, and selectivity to specific products) are needed. These improvements, along with new and more efficient routes to coal utilization, will come about only if we are able to gain more fundamental knowledge of coal in terms of its structure and reactivity.

The coal's inorganic structure and reactivity, as well as coal's organic extractability, are both important to coal conversion and utilization. Mineral matter plays a variety of important roles in all coal utilization processes. Chemical analysis of mineral matter in U.S. coals, usually expressed in terms of oxides as the weight percent in the high-temperature ash, have been widely available for years.[1] For the most part such analyses have usually emphasized the major (>1% of ash) and minor (<1% of ash) constituents. Traditional methods for the elemental analysis of bulk materials, such as atomic absorption (ASTM Methods D3682 and D3683) and inductively coupled plasma spectrometry, are typically solution-based techniques and can be used in coal ash analysis. These are tried-and-proven

successful analytical techniques; however, they require dissolution procedures that can be time-consuming. Dilution of the analyte and concomitant contamination sometimes result in lowered sensitivities, quantitative errors, and spectral interferences.

Direct solids techniques for nonconducting material analysis are quite powerful in some respects and do not require dissolution procedures. However, most of them are not free of analytically undesirable effects such as lateral spatial resolution, or lack the sensitivity for trace component detection.

Glow discharge provides a steady-state source of excitation and ionization that is relatively free of matrix effects due to separate atomization and excitation/ionization steps, which makes it an attractive and a relatively inexpensive source for nonconducting materials analysis.[2] The potential to use glow discharge-atomic emission spectrometry (GD-AES) for coal ash analysis is promising. Factors important to this methodology are sample preparation, sample composition, and the working conditions of the lamp.

The choice of conductive host matrix material is paramount to the success of the analysis. For good sensitivity, host materials with high sputter rates are desirable. In one study of clay samples,[3] emission intensities for the analyte elements were significantly higher when the clay sample was mixed with copper rather than either silver or graphite, which provided similar intensities. Other desirable characteristics of the host include good mechanical strength upon pressing, high thermal conductivity, low cost and availability in high purity, and a variety of particle sizes. Copper,[4] silver,[4] graphite,[5] tantalum,[6] iron,[7] nickel,[7] and a 4:1 (w:w) mixture of copper and graphite[3] have all been used successfully.

When choosing an appropriate sample/host composition, a trade-off between sputtering rate and analyte concentration must be considered. Maximum analytical signals are usually obtained at nonconductive material percentages of 20%. Most researchers agree on this percentage.[7, 8]

However, other percentages may be used successfully. For example, 10% samples were found to be optimal in one study involving the analysis of alumina-based automotive catalyst materials.[9]

Another important factor is the range of particle sizes present in the sample mixture. Small particle sizes are preferable. Homogeneity and discharge stability are usually the dominant concerns, and many researchers agree that particle sizes should be kept below approximately 30-40 μm in diameter in order to obtain acceptable accuracy and precision of analysis.[7,8]

Pre-sputter procedures are generally undertaken simply by allowing the analytical signals to stabilize at the discharge conditions desired for analysis before acquiring data. If large discharge powers are desired, such that sputter-induced heating is fast, the compacted sample may not be able to withstand the mechanical stress caused by the rapidly expanding trapped gases. An erratic discharge is usually the result. For this reason, pre-sputter methods in such cases should involve attaining the desired discharge conditions through several steps, each successive step employing a somewhat higher discharge power than the preceding step. This methodology has been demonstrated to be quite appropriate, though possibly time-consuming.

Determinations of analytes in nonconductive sample types compacted into host matrix materials have been done most often by comparison with suitably prepared external standards (i.e., through calibration curves). If the factors affecting a given analyte will similarly affect every analyte in the sample, then utilization of internal standardization is possible. Use of the host matrix material as the internal standard has met with mixed success. Determination of Ni using Cu as the internal standard was quite successful in one atomic absorption study.[4] Use of an additive (spike) as the internal standard, on the other hand, has been shown to be quite ap-propriate in several investigations.[8,9] Marcus and co-workers have demonstrated the successful use of Ba as an added internal standard in the determination of Pt and Rh in γ-alumina-based automotive catalyst materials by atomic absorption spectroscopy (AAS).[9] Average accuracy was improved by a factor of 6 for Pt and a factor of 9 for Rh by using the internal standard. In short, although glow discharge analysis of compact samples can be performed quite successfully with direct external standardization (calibration curves), it would appear that internal standardization might be a generally more attractive means of improving analytical determinations.

The first part of this study was to develop a method for the determination of major and minor elements in fluidized bed combustion (FBC) ashes by GD-AES. In addition to the mineral matter in coal and the coal ash, the organic compounds in coal or ash also play an important role in coal utilization. Solvent extraction has been one of the most commonly used techniques for studying the organic properties of coal. However, solvent extraction often requires more than 50% of the analyst's time and consumes large quantities of diverse hazardous organic solvents. As a result, interest in methods that use benign solvating media

such as supercritical fluids is increasing.[10] The main advantages of SFE over classical extraction methods such as the soxhlet extraction method are (a) less extraction time, (b) less solvent waste, and (c) the possibility of easily altering extraction conditions during extraction. Indeed, ease of use is one of the factors that has fueled widespread interest in the applicability of the technique to fields as diverse as pharmaceutical, polymer, food, and environmental sciences.[11]

SFE can be performed in a static, dynamic, or coupled static/dynamic mode. The static mode is often used when modifiers and derivatizing reagents are added, while a dynamic extraction, on the other hand, uses fresh supercritical fluid that is continuously passed over or through the sample matrix. The combination of a static extraction period followed by a dynamic one is gaining popularity, especially for situations in which analyte must diffuse to the matrix surface to be extracted.

Once the extraction vessel has been properly loaded with the sample, the various SFE parameters of fluid, density, pressure, temperature, and flow rate must be determined. Equally important are the trapping conditions, such as type, temperature, and rinse. The details of an actual method are usually instrument specific. The accepted protocols for restriction and trapping are debated continually (e.g., liquid vs. solid phase trap; fixed vs. variable restrictor). Because of differences in sample chemical composition, there is no universal trapping method that will work in all situations.[12, 13, 14] However, if analytes are bound to the matrix, greater solvating power or higher temperature is needed. Experimental considerations should then be explored in this order: raise supercritical CO_2 density, raise fluid flow rate, increase extraction temperature, and add modifier.

Much research has been performed over the last 25 years on producing liquid chemicals and fuels from coal by a variety of processes. Supercritical fluid extraction of coal[15] has received attention because of the greater dissolution power of the supercritical fluid compared to gases in conventional pyrolysis. Supercritical liquefaction typically involves the thermal breakdown of coal and subsequent dissolution of the pyrolysis products in the solvent. The solvents commonly used were toluene, tert-butanol, etc. The temperatures used were 593-673K or higher. Pressure was moderate to high (6-30 Mpa). The method shows potential for commercial application, although most studies have been limited to research on thermodynamics, chemical mechanisms, and the structure of the coal and extracts.[16] To our knowledge, there is very little or no published information on supercritical extraction of coal with pure CO_2 or methanol-modified CO_2 and at a temperature lower than 150°C. Because many commercial supercritical fluid extractors have the maximum use temperature of 150°C, it is necessary to do some fundamental extractions on coal at a temperature below 150 °C. The second part of this research is to study the feasibility of extracting organics from coal by supercritical CO_2 or methanol-modified CO_2 at temperatures below 150°C, to compare the results by SFE and soxhlet extraction, and to study which parameters affect the extraction efficiency most.

II. EXPERIMENTAL

A. Materials

In the GD-AES study, both graphite and copper were used as the host material. The concentrations of the constituents of the ash used are shown in Table 1. The graphite powder (Zeebac Inc.) and ash were ground to as small a particle size as possible and heated to 100°C for 3 hours before mixing. The copper powder (Alfa AESAR) was 99.5% grade, with a size of 150 mesh or a smaller size of 325 mesh. The Cu was ground with ash in an agate mortar and pestle, then the mixture heated to 100°C in a vacuum for 3 hrs.

Table 1. Concentrations of Major and Minor Constituents in the Ash Samples

Sample	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O_3	P_2O_5	SiO_2	TiO_2
NIST 1633a	27.03	1.55	13.44	2.27	0.75	0.0283	0.23	-----	48.77	1.33
BCS 382/I	3.79	40.1	28.5	----	3.73	7.96	---	3.06	13.03	0.42
BCS 382	7.51	33.0	16.59	----	10.7	9.2	----	1.23	19.5	0.50
NIST 76a	38.7	0.22	----	1.33	0.52	----	0.07	0.12	54.9	2.03
NIST 77a	60.2	0.05	----	0.09	0.38	---	0.037	0.092	35	2.59
NIST 78a	69.22	0.11	----	0.11	1.12	---	0.078	1.3	19.4	3.22

In the study of soxhlet extraction and SFE, IBC-103 (or WKU No. 89022) was used as the coal sample. The analytical values for this sample are shown in the following table.

Table 2. Dry Basis Analytical Values for Coal Sample 89022

Parameters	Value, %
Moisture	5.72
Vol Matter	36.31
Fixed C	55.01
H-T Ash	8.62
Carbon	74.53
Hydrogen	4.91
Nitrogen	1.72
Oxygen	7.63
Sulfatic sulfur	0.00
Pyritic sulfur	1.00
Organic Sulfur	1.11
Total Chlorine	0.10
FSI	5.01
Btu/lb	13442.59

The solvents commonly used are 2-methylpyridine, 2,6-dimethylpyridine, N,N-dimethylformamide, triethylamine, dichloromethane, and tetrahydrofuran (THF). The solvent 2-methylpyridine has been proven to be the best solvent among these, and was chosen as the solvent in this research.

B. Instrumentation

1. The Radiation Source for GD-AES.

The glow discharge source used in the SA-2000 spectrometer is a water-cooled Grimm type with a standard 8 mm lamp, which is shown schematically in Figure 1. The sample pellet, used as part of the cathode, is sealed into the lamp body by means of the o-ring. The argon gas enters the lamp and leaves by two pumps which maintain the vacuum condition for the system.

Figure 1. Grimm type lamp used in the SA-2000 spectrometer.

2. The GD-AES Spectrometer

The SA-2000 spectrometer is a 0.4 meter direct reader that features a 0.55 nm/mm first order dispersion, and a spectral range of 150 to 456 nm. Optional wavelength extensions are available for non-metal elements. The classical Paschen-Runge configured spectrometer (Figure 2) permits up to twenty-eight output channels. The output of each channel corresponds to the intensity of emission from a particular element. The elements which the SA-2000 can currently analyze include Ag, Al, As, C, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Se, Si, Ti, W, Zn and Zr. The raw intensities versus time are collected using a computer equipped with fast digital signal processing hardware.

Figure 2. The classical Paschen-Runge configured SA-2000 spectrometer.

3. Soxhlet Extractor

Solvent extraction of coal has been established and utilized extensively as a convenient method in the study of coal structure and the chemical characterization of coal. Soxhlet extraction is one of the most widely used solvent extraction techniques. The soxhlet extraction apparatus is shown as Figure 3.[17] The coal sample is placed in the extraction thimble (made of heavy filter paper-type material), and the extraction solvent is placed in the flask. When brought to reflux, the solvent is condensed onto the material in the thimble. When the solvent level in the thimble reaches the same level as the top of the siphon arm, the entire liquid content (consisting of a dilute solution of the extracted material) of the thimble is siphoned into the flask.

Figure 3. The soxhlet extraction apparatus.

4. Continuous Flow Systems in Supercritical Fluid Extractor.

SFE can be performed in a static, dynamic, or coupled static/dynamic mode. A static

extraction takes place when a fixed amount of SF interacts with the analyte and the matrix.

A dynamic extraction, on the other hand, uses fresh SF that is continuously passed over or

through the sample matrix, as shown in Figure 4.

C. Experimental Procedures

1. Sample Cathodes for GD-AES.

For GD-AES analysis, sample cathodes were pressed from a mixture of the appropriate

powders with a die press assembly. The powders and their pretreatments were introduced

in section A. The force used to press the powders was approximately 20 tons. The face

which was sputtered to form an atomic vapor of the constituents was 3.2 cm or 1.28 cm in

diameter.

The pellet is placed in the sample holder, and the latter inserted into the lamp, which

is then evacuated. When the pressure reaches a predetermined level, the gas control unit

automatically switches a set of relays which adjusts the gas flow and gas pressure in the

lamp. Initial sputtering of the sample surface is required before measurement of intensity

may be made. The preburn is used to clean the surface of any impurity, such as absorbed gas

atoms, which may be present.

Dynamic Extraction Run Sequence

START1 or START2 softkey is pressed

Pump Pressure
The vent valve closes and the Pump(s) starts. The SFX 200 Controller will display:
"WAITING PRESS"
until user set pump pressure is reached.

Flow Equilibration
Controller will display:
"WAITING FLOW"
until equilibration flow rate is less than the user set value.

Extraction Temperature
The SFX 200 Controller will display:
"WAITING HEAT"
until the user set extraction chamber temperature is reached.

Once the pressure, flow, and temperature conditions are met, the supply valve will open. The pressure will drop while the extraction chamber fills and the SFX 200 Controller will display:
"PRESSURIZING".

Equilibration Time
Once the extraction chamber is filled and pressurized, the message:
"STABLIZING"
will be displayed while the user set equilibration time elapses.

Dynamic Extraction Time or Volume
The analyte valve then opens and waits for user set dynamic extraction time or volume. The first limit reached will end the extraction.

The analyte valve closes.

The supply valve closes.

The vent valve opens and the VENTING LED on top of the extractor lights.

After the run in the chamber is complete, the words:
"STOPPED"
will be displayed.

Labels in diagram:
SFX 200 Controller
CO2 Pump
Supply Valve
Extraction Chamber
Sample Cartridge
Sample
Vent Valve
Analyte Valve
Restrictor Fitting
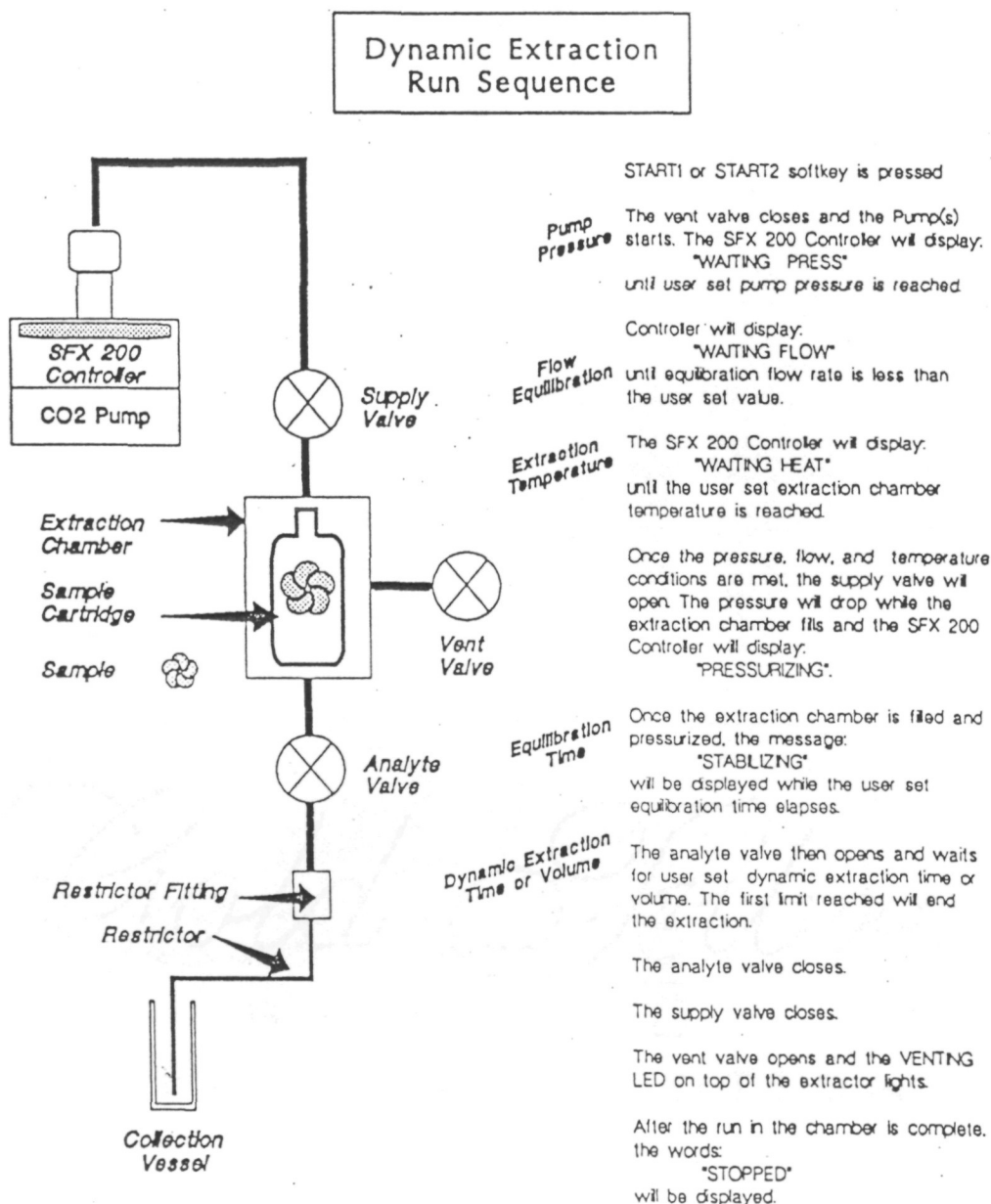Restrictor
Collection Vessel

Figure 4. Continuous flow systems in a supercritical fluid extractor.

2. Soxhlet Extraction Procedure

The following procedure[18] was used for the drying, extracting, rinsing, and redrying of each coal, using standard soxhlet extraction assemblies at the atmospheric reflux temperatures of the solvent employed, 2-methylpyridine (2-picoline).

a. Oven dry 100 mL beakers, cool in a desiccator, and weigh to the nearest mg. (All subsequent weighings are to the nearest mg.)

b. Add to each beaker approximately 10 g of powdered coal (-60 mesh), without predrying. Weigh, then place samples in a vacuum oven at 60±4°C for a period of six hours. Allow the temperature to drop to less than 50°C to prevent rapid air oxidation, remove samples to desiccator, cool to room temperature and reweigh to obtain moisture loss.

c. Concurrently with step 2, mark cellulose soxhlet thimbles, vacuum dry with the coal, cool in desiccator, and weigh. Transfer the dry coal samples to the thimbles and weigh again.

d. Set up the soxhlet extraction apparatus units, load the coal-containing thimbles, charge the 250 mL flasks with 150 mL of 2-methylpyridine. Insulate the glass assembly below the condenser so that most of the heat loss occurs in the condenser. Carry out reflux extraction 20 to 24 hours.

e. Collect the 2-methylpyridine extract from flasks. Add 150 mL of methanol to flasks, reassemble, and carry out reflux rinsing of the coal residue for 5 to 6 hours.

f. Remove soxhlet thimbles, allow free solvent to drain away and air dry samples (to prevent blowouts of coal powder under vacuum drying). Place in vacuum desiccator, evacuate for about 30 minutes, and allow to stand overnight.

g. Transfer to vacuum oven and dry at 150°C for a period of six hours. Allow temperature to drop to 50°C, remove samples to cool in desiccator, and weigh to obtain extraction loss.

h. Replace samples in vacuum oven and dry at 150°C for two hours. Allow temperature to drop to less than 50°C, remove samples to cool in desiccator and weigh. Repeat this step until constant weight is obtained. The third weighing usually provides a good verification of the second weighing.

i. Store coal residues in airtight vials at freezer temperature. Calculate percent weight loss due to moisture (step b) and percent weight loss by solvent extraction of the moisture free coal.

The 150°C final vacuum drying temperature was employed to remove the significant amount of the nitrogen-base extractant retained after extraction owing to the great affinity of extracted coal residue for nitrogen compounds.

3. Sample Pretreatment for SFE.

The 83013 coal used in this research was prepared by sieving to a particle size range of (35-60 mesh). Investigators at NCB reported that the particle size did not significantly affect the experimental results under 8 mesh (smaller than 2.36 mm).[19] Hershaw[20] reported that for coal particle sizes below 1.6×10^{-3} m, there was little relation between the conversion

and particle size, and there was no tendency to agglomerate if the particle size was larger than 2.0×10^{-4} m.

The coal samples were sealed and stored in a refrigerator to prevent oxidation, and before extraction were vacuum-dried at 343K for six hours. A small amount of methanol was added to the dried coal samples, and after shaking the mixture of the coal and solvent for 40 minutes at 313K, the solvent was poured out and fresh methanol was added. This procedure, which removes some highly soluble compounds from the coal, was repeated 3 to 4 times. The coal samples were vacuum-dried again at 343K and weighed. Sand, which was added to the sample, was also pretreated the same way as the coal. The dried coal particles were then stored in desiccators and were used after moisture content determination through thermogravimetric analysis (TGA).

III. RESULTS AND DISCUSSION

A. The Determination of Inorganic Constituents in Coal Ash.

1. The Composition of the Samples and Their Characteristics.

Both graphite and copper were used as the host material as shown in Table 3. In some studies, wax and detergent were also used as the binder. From Table 4, one can see that the pellets using graphite as the host material (conductive material) is very smooth, which can both hold the vacuum and conduct current very well even when as little as 20% graphite is used. Copper is difficult to mix well with the ash. Since the surface is not uniform and smooth, the pellets can not hold the vacuum well and the conductivity is bad. When wax or detergent was used as the binder, the surface of the pellets was smooth enough. However, wax or detergent can absorb emissions during burning and even make continuation of the analysis difficult. By using small particles of copper and ash, the pellets can also be made smooth and homogeneous enough.

2. Sample with Graphite as the Matrix Host Material.

a. The Preburn Process. Compacted ash samples contain large amounts of gases including water vapor. Disk preparation traps residual gases in the sample and host matrix powder. The temporal response of the plasma emission can be affected during evolution of these gases as the sample is heated by the sputter process.

Table 3. The Percent Composition of the Pellets Prepared

Number	Cu	Graphite	Ash	Wax	Detergent
1	90	10	---	---	---
2	90	5	5	---	---
3	90	---	5	---	5
4	80	---	20	---	---
5	80	---	15	5	---
6	80	---	15	---	5
7	60	---	30	10	---
8	50	---	40	10	---
9	50	---	40	---	10
10	47.5	---	47.5	5	---
11	47.5	---	47.5	5	---
12	45	---	45	10	---
13	45	---	45	---	10
14	40	---	55	5	---
15	40	---	55	---	5
16	---	90	10	---	---
17	---	90	5	5	---
18	---	90	5	---	5

--- Continued ---

Table 3. Continued

Number	Cu	Graphite	Ash	Wax	Detergent
19	---	80	15	5	---
20	---	60	35	5	---
21	---	60	35	---	5
22	---	47.5	47.5	5	---
23	---	45	45	10	---
24	---	45	45	---	10
25	---	40	50	10	---
26	---	40	50	---	10
27	---	20	70	10	---
28	45	10	40	5	---
29	45	10	40	---	5

Table 4. The Characteristics of the Pellets Prepared

Number	Vacuum	Voltage	Current	Ω
1	0.25-0.48	1.82	0.32-0.34	0.03-0.5
2	0.18	1.82	0.31	0
3	0.19	1.82	0.31	0
4	0.21-0.24	1.82	0.31	0.01-∞
5	0.18	1.83	0.31	0.02-∞
6	0.18	1.83	0.31	0
7	0.18	1.83	0.31	∞
8	0.18	1.82	0.31	∞
9	0.18	1.83	0.31	∞
10	0.18	1.82	0.31	∞
11	0.18	1.82	0.31	∞
12	0.18	1.82	0.31	∞
13	0.18	1.82	0.31	∞
14	0.18	1.82	0.31	∞
15	0.18	1.82	0.31	∞
16	0.19	1.82	0.31	0
17	0.18	1.82	0.31	0

--- Continued ---

Table 4. Continued

Number	Vacuum	Voltage	Current	Ω
18	0.18	1.82	0.31	0
19	0.18	1.82	0.31	0
20	0.18	1.83	0.31	0
21	0.18	1.82	0.31	0
22	0.18	1.83	0.31	0
23	0.18	1.82	0.31	0
24	0.18	1.82	0.31	0
25	0.18	1.83	0.31	0
26	0.18	1.82	0.31	0
27	0.18	1.82	0.31	0
28	0.18	1.82	0.31	0.02
29	0.18	1.82	0.31	0.02

Initiation of the discharge at high currents can cause plasma instability and possibly sample disk fracture. Figure 5 shows the temporal response of voltage (V), current (I), and pressure (P) during burning of a disk at I = 40 mA without preburn. Figure 6 shows the temporal response of Ca, Al and Si emission from the same burning process. Because of the fast out gasing process, the current and pressure can not maintain stability, causing signals of all elements to be unstable.

Figure 7 shows the V, I and P response during burning on the same disk as above at I = 40 mA after a preburning process which operates at I = 20 mA for 100 s. It is obvious that the current is very stable if a suitable preburning process is added. For all subsequent studies, initiation of the discharge was at 20 mA for 2 minutes, followed by an increase to the working current needed for analytical data acquisition.

   b.   Effect of the Power on the Intensities of Emission.   The current has a profound effect on the intensities of the emission. The higher the current, the larger the intensities of the emission. Figure 8 and Figure 9 compare the response of Si, Mg , Fe, Al and Ca emissions from a 10% ash standard 382/graphite matrix sample at different working currents. The intensities of Al and Si at I = 50 mA are almost 10 times those for I = 10 mA. The voltage also affects the intensities greatly. The higher the voltage, the larger the intensities. However, too high a voltage will make the signals unstable and even cause the burning process to stop.

Figure 10 shows the response of Ca, Al and Ti emission from a 10% ash standard 382 at currents of 50, 55 and 60 mA. The responses of V, I and P are shown in Figure 11. It seems that the intensities do not change much when the current is above 50 mA.
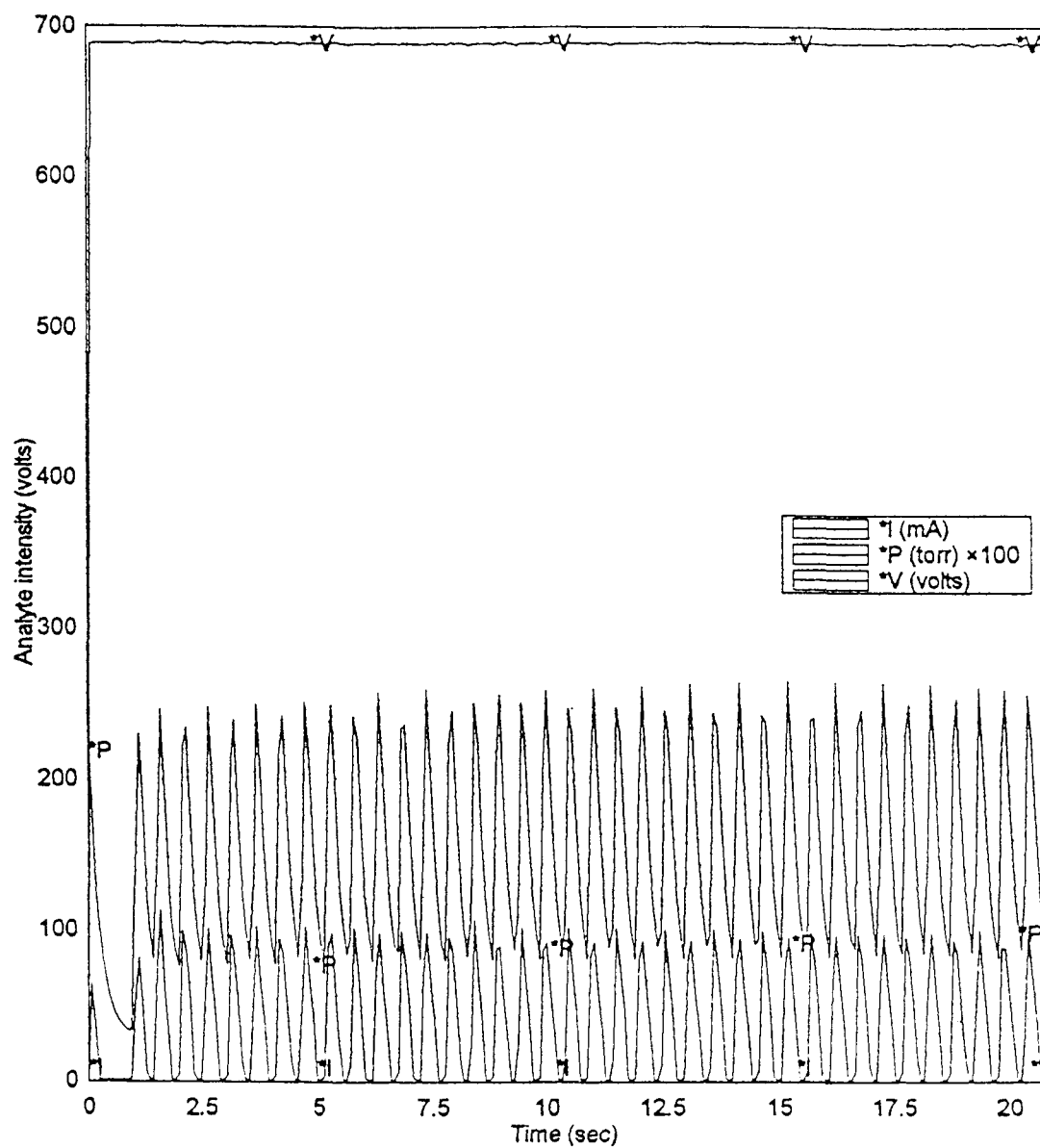
Figure 5. The temporal response of V. I and P during burning on a 10% ash standard 382/graphite matrix sample without preburning. The current is 40 mA and the voltage is 700 v.
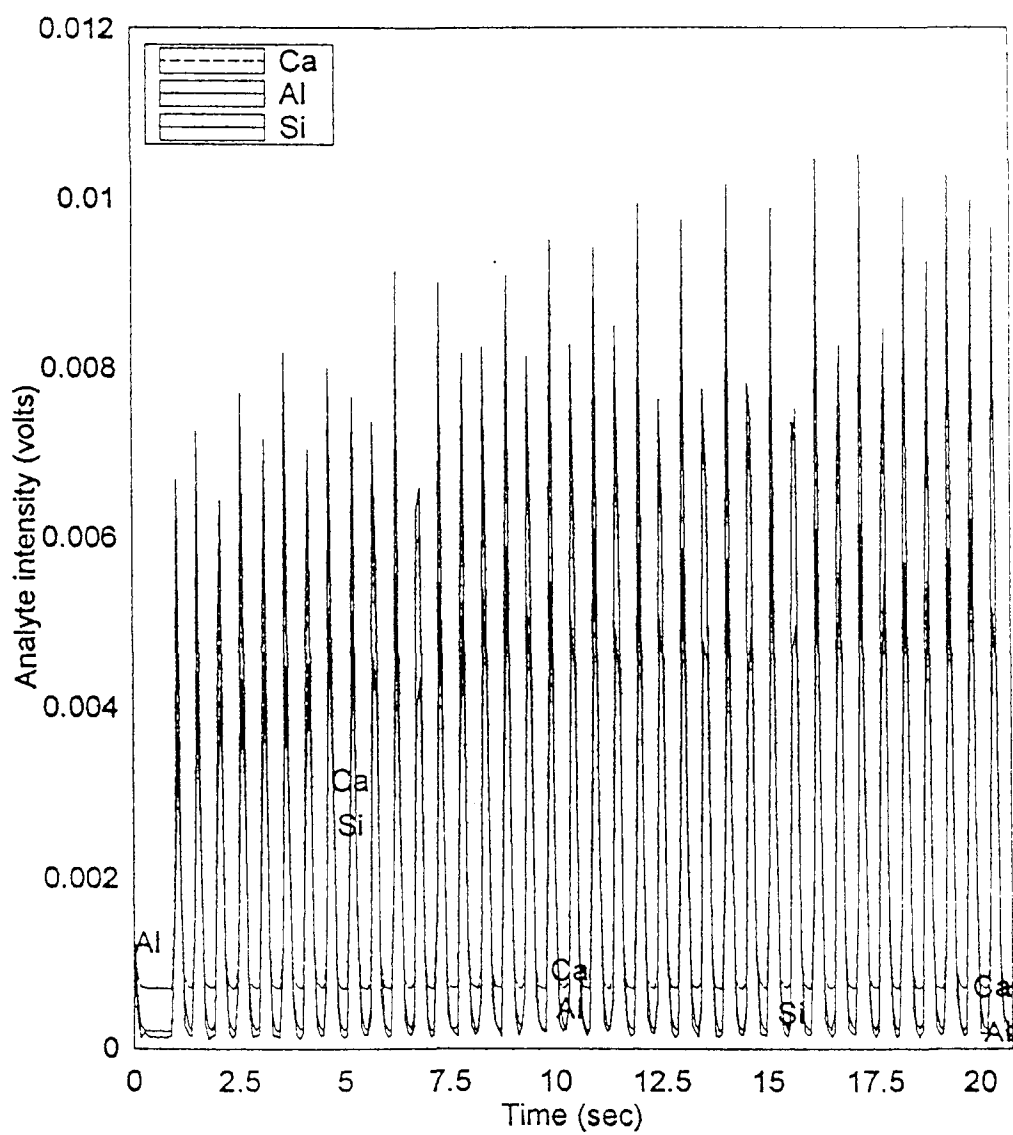
Figure 6. The response of Ca, Al and Si emission from 10% ash standard 382/graphite matrix sample without preburning. The current is 40 mA and the voltage is 700 v.
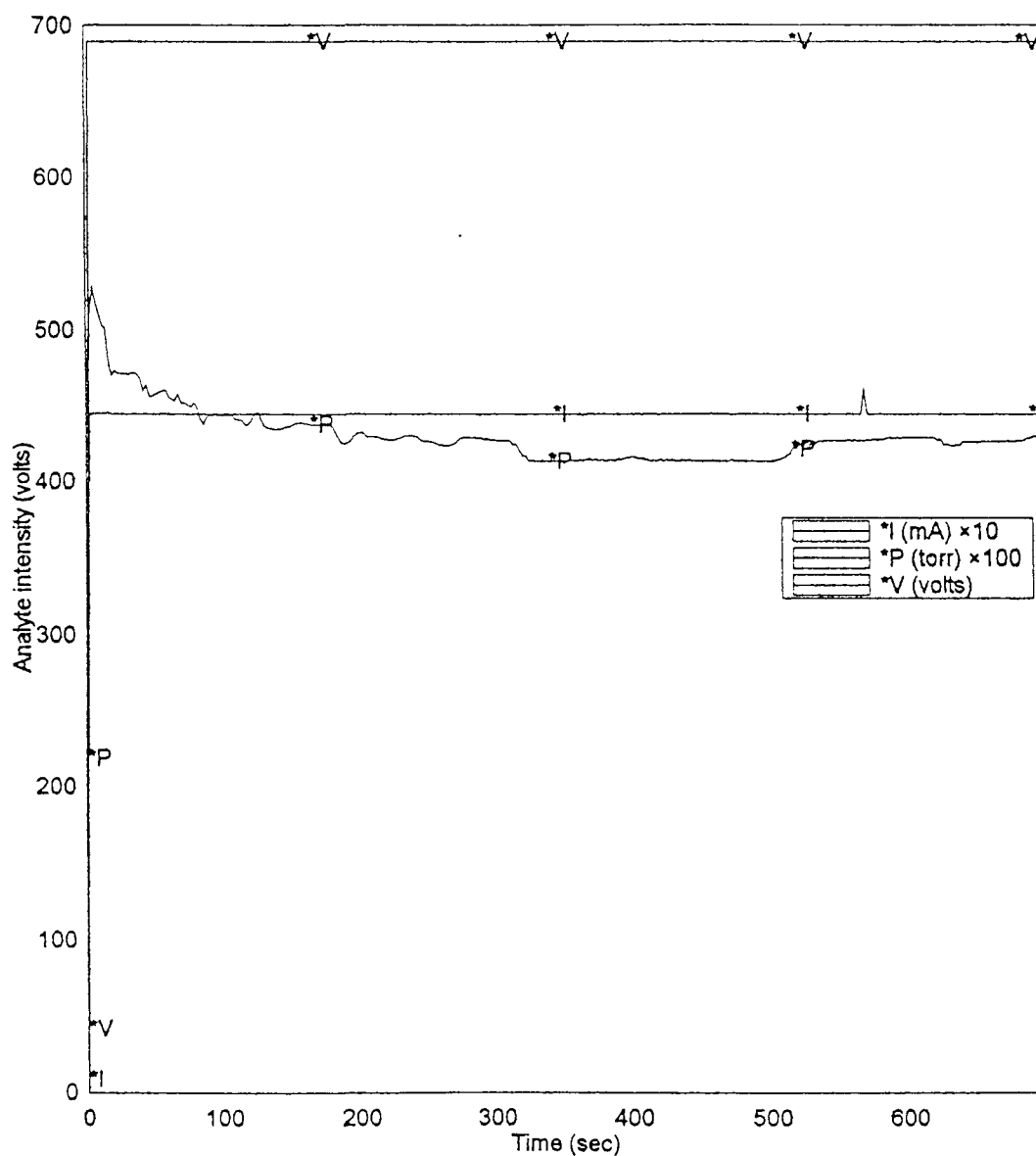
Figure 7. The temporal response of V, I and P during burning on the same disk as in Figures 5 and 6. The current is 40 mA and the voltage is 700 v. The preburning current is 20 mA and the voltage is 700 v.

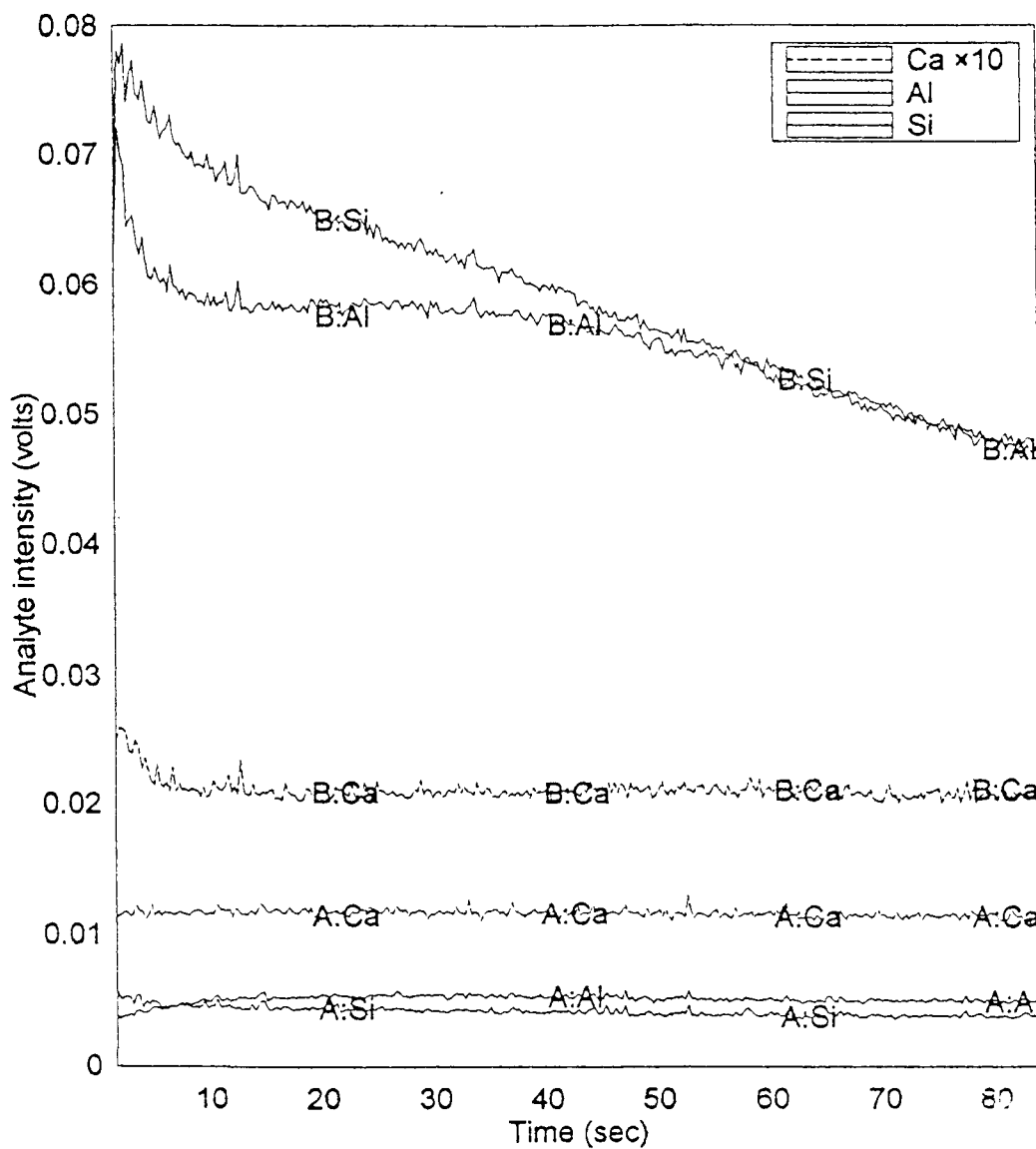Figure 8. The response of Si, Al and Ca emission from 10% ash standard 382/graphite matrix sample. (A) The current is 10 mA and the voltage is 700 v. (B) The current is 50 mA and the voltage is 700 v.

Figure 9. The response of Mg and Fe emission from 10% ash standard 382/graphite matrix sample. (A) The current is 10 mA and the voltage is 700 v. (B) The current is 50 mA and the voltage is 700 v.

Figure 10. The temporal response of Ca, Al and Ti emission from a 10% ash standard 382/graphite matrix sample. (A) The current is 60 mA. (B) The current is 55 mA. (C) The current is 50 mA. The voltage is 700 v.
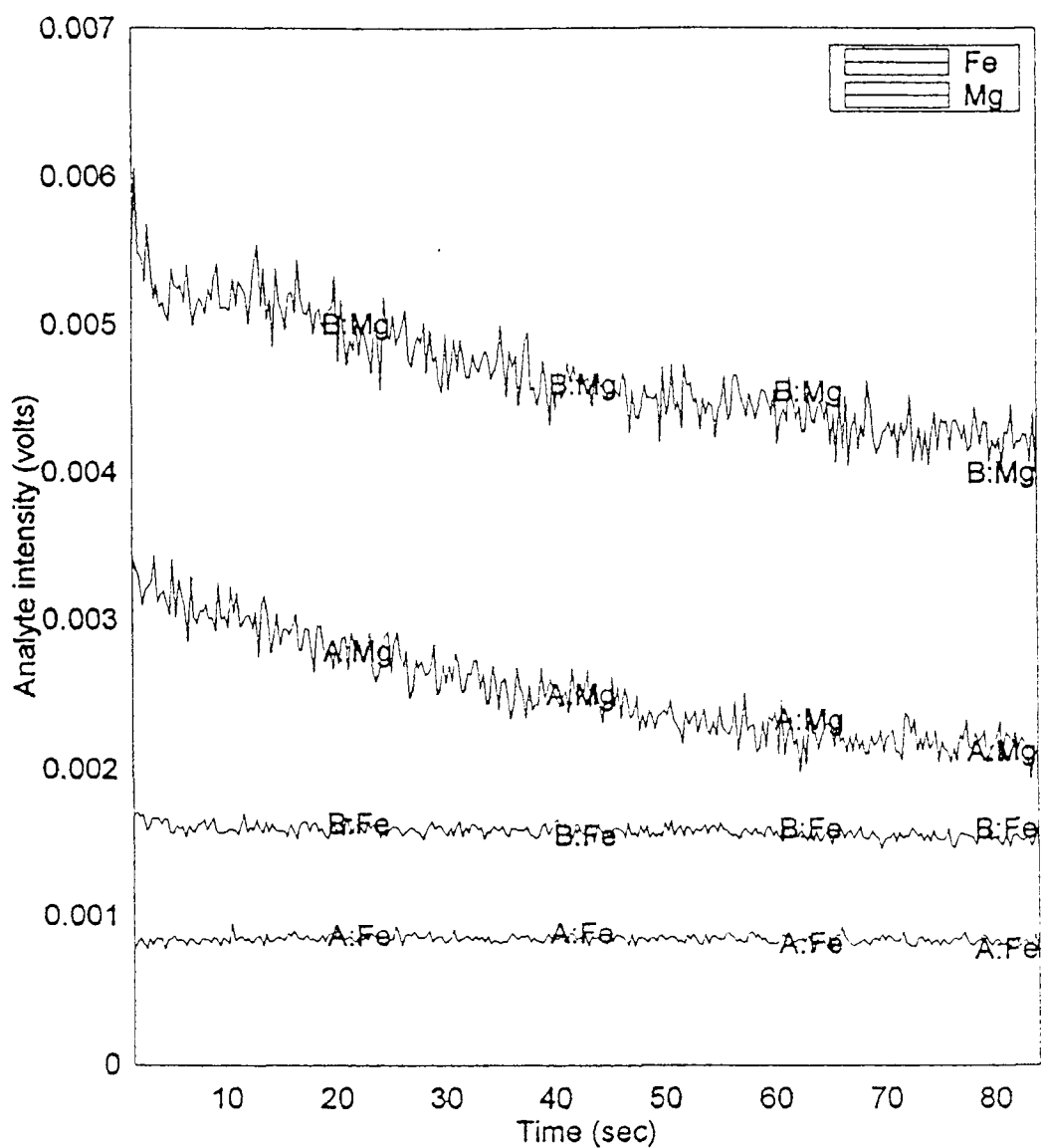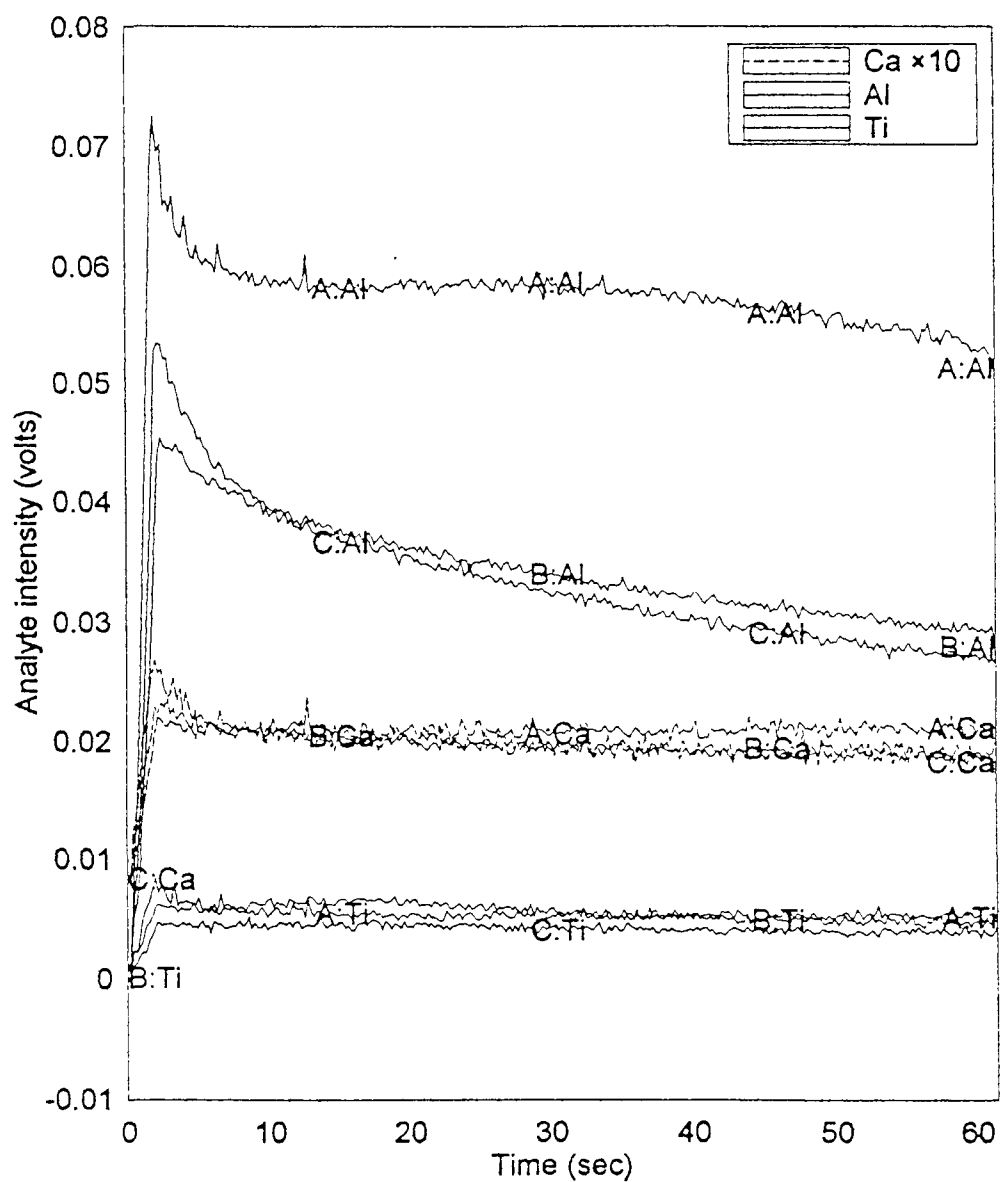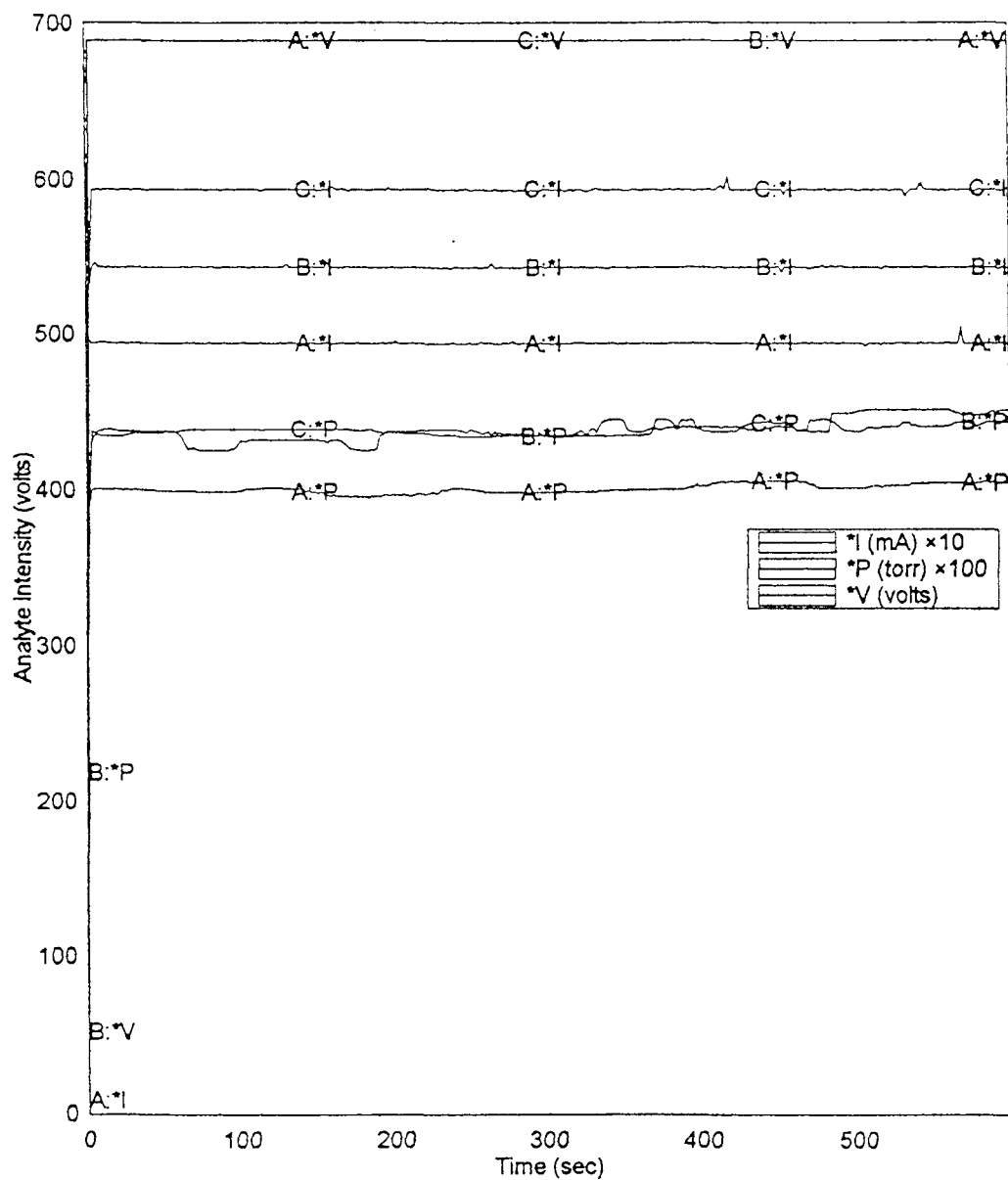
Figure 11. The response of V, I and P during the same burning process as Figure 10. (A) The current is 50 mA. (B) The current is 55 mA. (C) The current is 60 mA. The voltage is 700 v.

Figure 12 shows the effect of preburn current on the intensities of Ca, Al and Ti. The value of preburn current has little effect on the intensities, indicating that I = 20 mA and U = 700 v for 120 s is enough for out gasing of the compacted sample.

The repetition of analysis for the compact graphite sample has been demonstrated as shown in Figure 13. In these two analyses, the intensities of S and Fe are fairly close to each other. The intensities of Al are much different at first, but they come close after about 400 seconds. The same is true for Ca and Mn.

c.   The Calibration of the Graphite Based Standard Samples. From the above study, we can see that when the current is above 50 mA, the intensities of the elements will change very little with the current. From Figure 13, we can see that the intensities of the same element by two different analyses come close after about 400 seconds. In the following calibration process, we choose I = 50 mA and U = 700 v as analysis conditions after 420 seconds of preburn at the same current. We choose 21 w and vacuum = 3.12 torr as the pre-start condition, which has the same effect as I = 20 mA for the preburn above.

The analyte wavelengths chosen are as follows: Ti, 338.289 nm; Si, 288.158 nm; Mg, 383.829 nm; Al, 396.152 nm; Ca, 393.367 nm; Fe, 371.994 nm; Mn, 403.449 nm; C, 165.701 nm; P, 177.499 nm. Two types of calibration modes were used, normal and normalized methods. The normal mode graphs concentration versus intensity, while the normalized mode graphs (analyte concentration/matrix concentration) versus (analyte intensity/matrix intensity). Graphite was chosen as the matrix element.

Figure 12. The response of Ca, Al and Ti emission during a burning process after pre-burning;
(A) with preburning current of 30 mA, (B) with preburning current of 20 mA for 120 seconds.

Figure 13. The repetition for compact graphite sample. (A) and (B) are burning results on two different spots of the same sample, which is made up of 90% graphite and 10% standard (382). The current is 50 mA and the voltage is 700 v.

The results of calibration for Si and Al using normalized modes are shown in Table 5 and Table 6, respectively. Figure 14 and Figure 15 show the calibration curves for Si and Al, respectively. The average percentage error between the calculated and certified values was about 5%.

Table 5. The Results of Calibration for Si.

Standard	Intensity	Calculated	Certified	Difference	% Error
NIST 77a	0.01317	3.851	3.500	0.3514	10.04
NIST 78a	0.006522	2.069	1.940	0.1293	6.663
NIST 1633a	0.01573	4.540	4.877	-0.3366	-6.901
BSC 382	0.005809	1.869	1.950	-0.08066	-4.136
NIST 76a	0.01937	5.521	5.490	0.03123	0.5689
BSC 382/I	0.003354	1.208	1.303	-0.09469	-7.267

Standard	Runs	Std. Dev	Weight	Sputter Rate	Weight Factor
NIST 77a	2	0.002	1.000	0.3750	1.000
NIST 78a	3	0.0005	1.000	0.3750	1.000
NIST 1633a	2	0.0007	1.000	0.3750	1.000
BSC 382	2	0.0008	1.000	0.3750	1.000
NIST 76a	2	0.00002	1.000	0.3750	1.000
BSC 382/I	2	0.0002	1.000	0.3750	1.000

Figure 14. The calibration curve for Si. The "reported" values refer to the intensity of the emission signals of Si. The "certified" values refer to the values accepted as the standards.

Table 6. The Results of Calibration for Al.

Standard	Intensity	Calculated	Certified	Difference	% Error
NIST 77a	0.04860	6.444	6.020	0.4235	7.035
NIST 78a	0.05201	6.918	7.170	-0.2517	-3.511
NIST 1633a	0.02201	2.740	2.703	0.03683	1.363
BSC 382	0.007861	0.7700	0.7510	0.01903	2.534
NIST 76a	0.0278	3.546	3.870	-0.3239	-8.370
BSC 382/I	0.005745	0.4753	0.3790	0.09628	25.40

Standard	Runs	Std. Dev	Weight	Sputter Rate	Weight Factor
NIST 77a	2	0.005	1.000	0.3750	1.000
NIST 78a	3	0.006	1.000	0.3750	1.000
NIST 1633a	2	0.002	1.000	0.3750	1.000
BSC 382	2	0.001	1.000	0.3750	1.000
NIST 76a	2	0.0008	1.000	0.3750	1.000
BSC 382/I	2	0.0009	1.000	0.3750	1.000

15. The calibration curve of Al using normalized mode. The "reported" values refer to the intensity of the emission signals of Al. The "certified" values refer to the values that has been accepted as the standards.

3.   Sample with Copper as the Matrix Host Material

a.   The Comparison of Copper and Graphite as the Matrix. The smaller particle size
of graphite results in better mixing characteristics but countered by its lower sputter rate
compared to copper. Comparisons were made by running two replicate disks of each matrix
type in a 9:1 mixture with the ash (standard 382). The response of Al, Mg, Si, Ca, Ti and Fe
emissions are shown in Figures 16 and 17. The intensity of Ca in the copper sample is
almost 100 times that in the graphite sample. The intensities of Al, Mg, Ti and Fe from the
copper pellets are also much larger than from graphite pellets. Copper serves as the most
attractive alternative in that it exhibits a high sputter rate that is less significantly altered by
the added sample volume.

Table 7. The Current and Voltage Used for Nine Experiments.

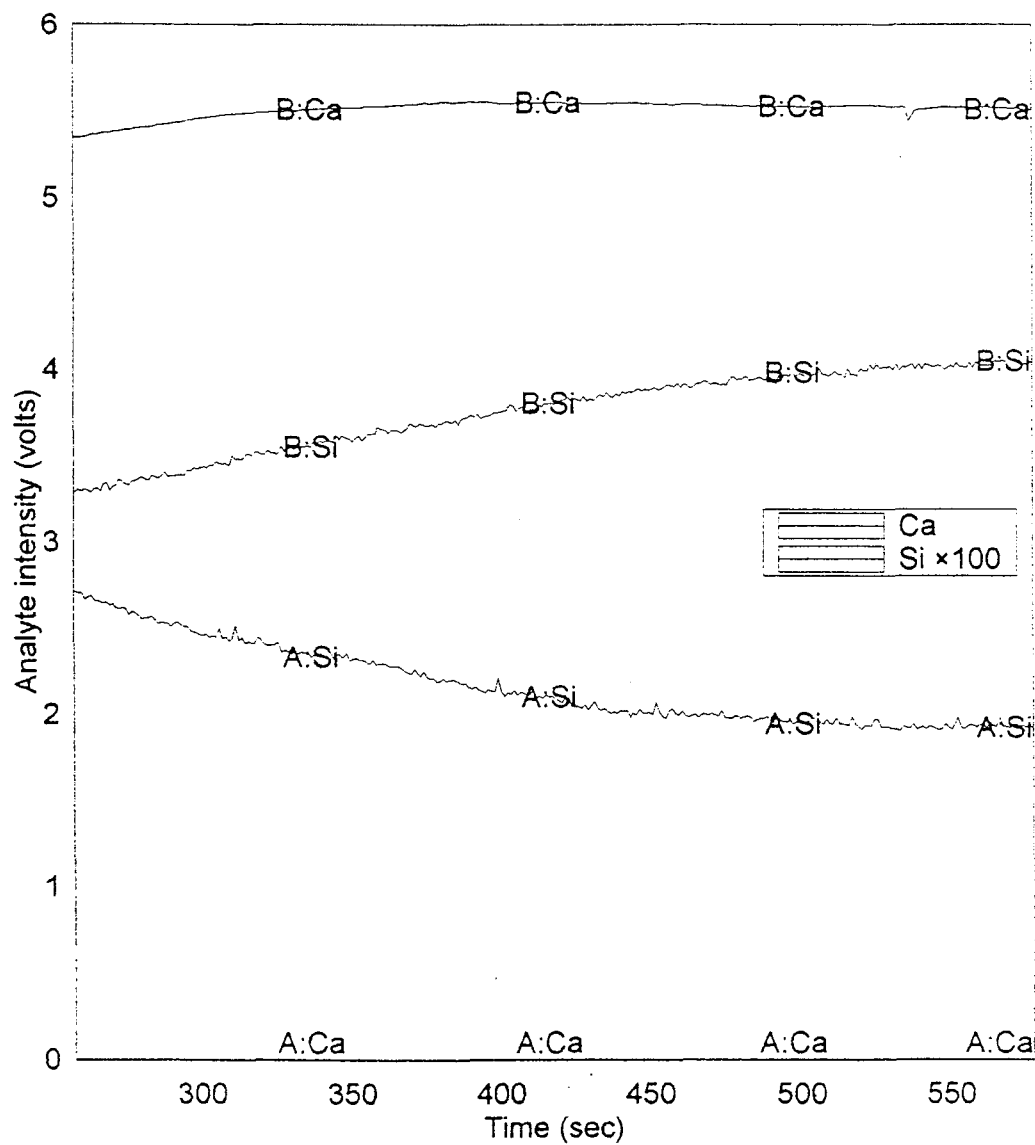| Number	Current I (mA)	Voltage V (v)
1	30	500
2	30	700
3	30	900
4	45	500
5	45	700
6	45	900
7	60	500
8	60	700
9	60	900

Figure 16. The response of Ca and Si emissions from (A) 10% ash standard 382/graphite matrix sample (B) 10% ash standard 382/copper matrix sample. The current is 50 mA, the voltage is 700 v.
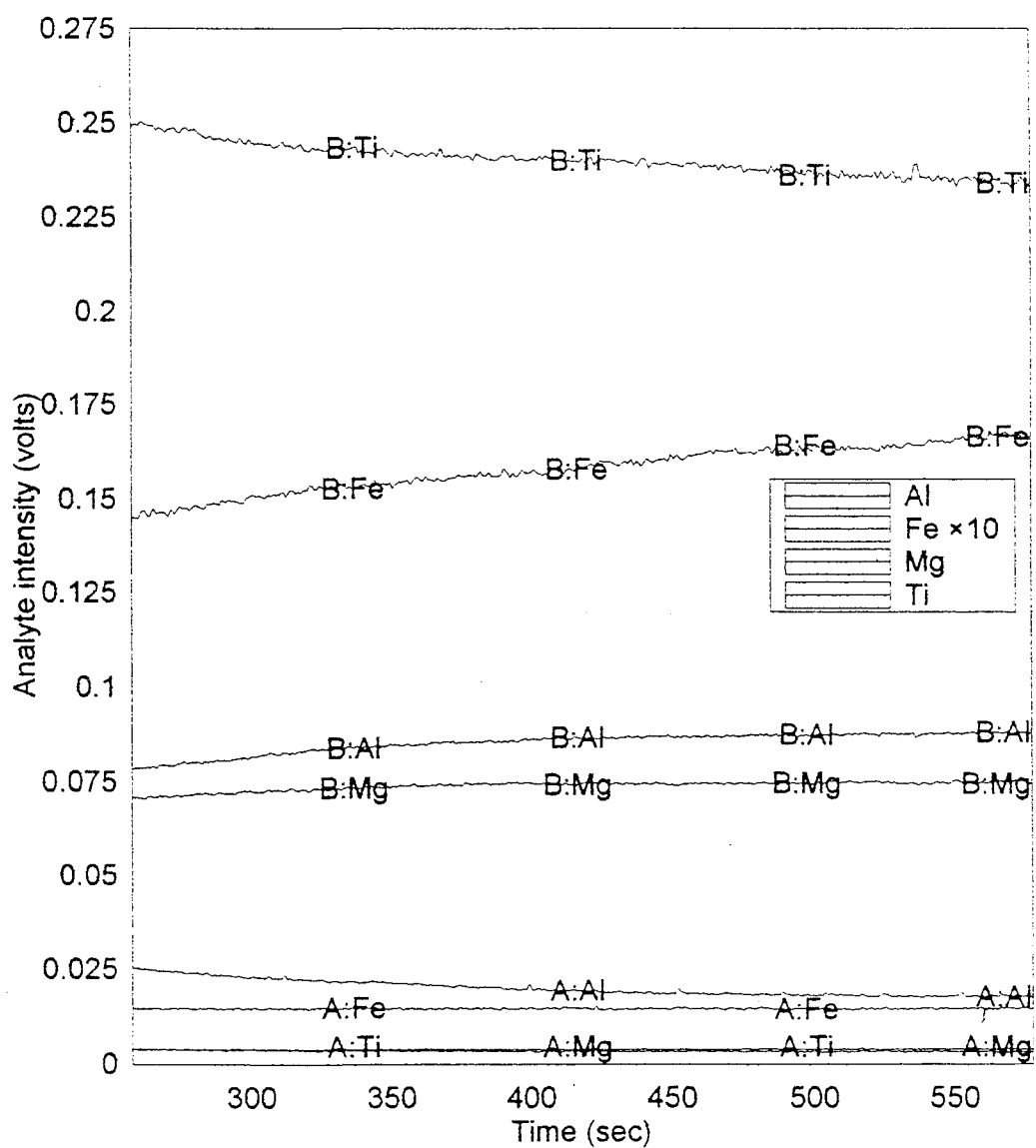
Figure 17. The response of Al, Mg and Ti emissions from (A) 10% ash standard 382/graphite matrix sample (B) 10% ash standard 382/copper matrix sample. The current is 50 mA, the voltage is 700 v.

b. <u>The Choice of Working Conditions for Copper Samples</u>. In order to study the effect of working current and voltage on the intensity of the emissions from various elements, nine experiments were devised, as shown in Table 7. The temporal response of Al, P and Si emission from the copper matrix sample in the conditions for experiments 1, 2 and 3 are combined in Figure 18. The results for the conditions of experiments 4, 5 and 6 are shown in Figure 19. Figure 20 shows the response of Al, P and Si emission from the same sample for the conditions of experiments 7, 8 and 9. One can see that the higher the current the larger the intensities of the elements. At 900 v, the intensity of Si emission at 60 mA is 2.2 volts, 1.5 times that at 45 mA, which is 1.4 volts and almost 30 times that at 30 mA. Al is the most difficult element among the three for analysis, since its emission intensity increases with time and it is hard to get a stable signal when 500 volts or 700 volts are used even if at a large current. However, when 900 volts were used, the signal stabilized around 300 seconds, no matter the current used. Higher voltage does not increase the intensity of Al as much as the current, but it does favor the stabilization of the signal. The same is true for all elements that have been studied.

Figure 18. The comparism of temporal responses of Al, P and Si emissions from a 10% ash/copper matrix sample in different conditions as listed as experiments 1, 2 and 3 in Table 7.

Figure 19. The comparism of temporal responses of Al. P and Si emissions from a 10% ash/copper matrix sample in different conditions listed as experiments 4, 5 and 6 in Table 7.
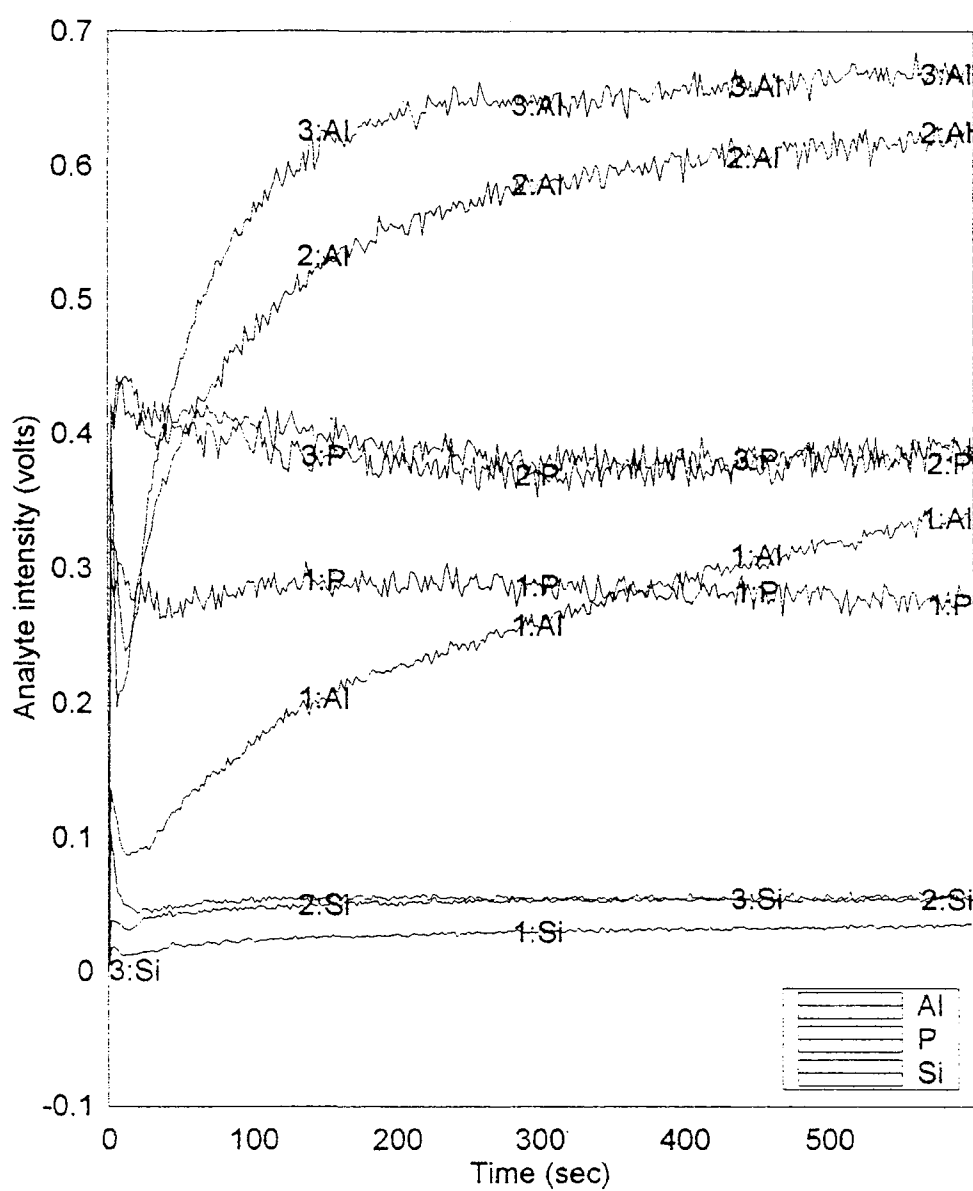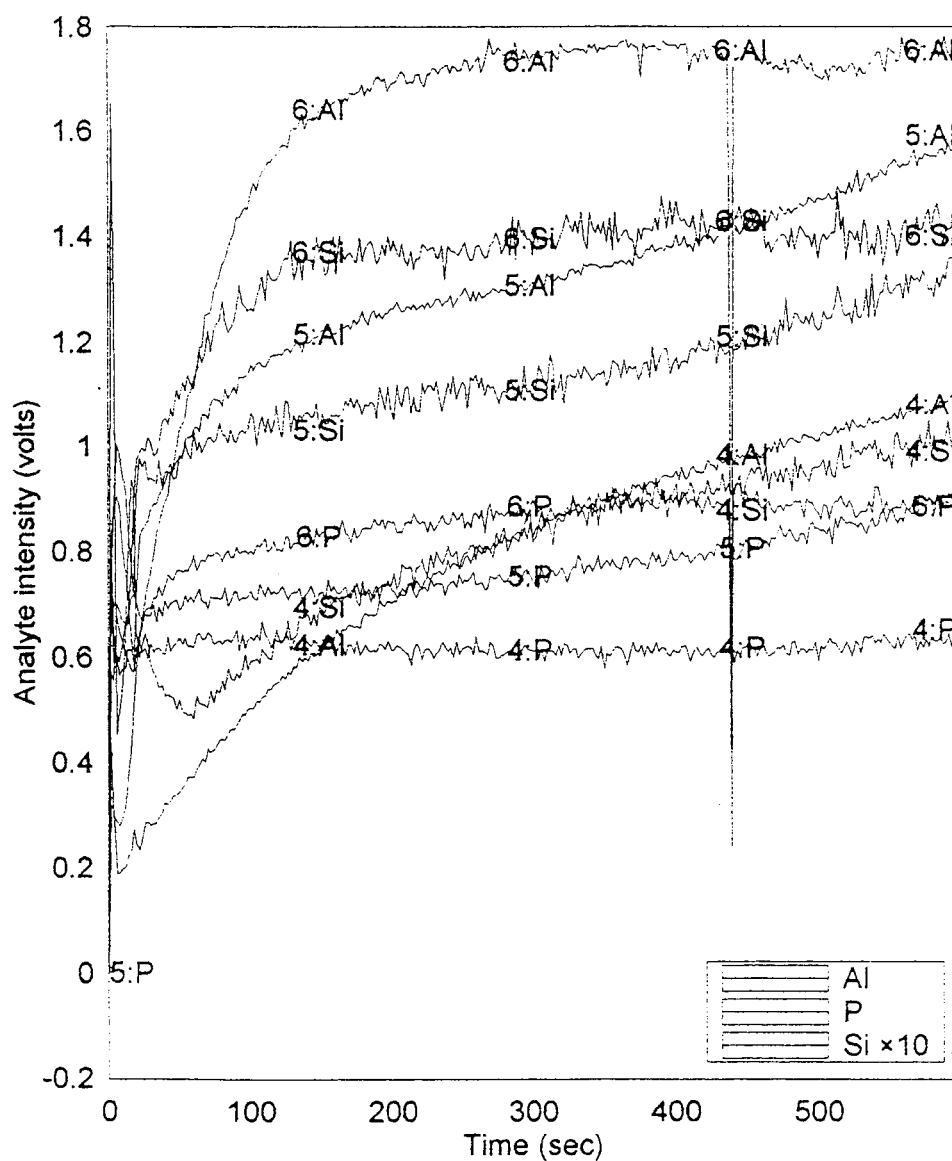
Figure 20. The comparism of temporal responses of Al, P and Si emissions from a 10% ash/copper matrix sample in different conditions listed as experiments 7, 8 and 9 in Table 7.

B.   Extraction of Hydrocarbons or Hydrocarbon Residues in Coal and Fly Ash

1.   Soxhlet Extraction

Table 8 lists the results of the coal run in triplicate with 2-methylpyridine.

Table 8.   Coal Fractions Extractable by 2-methylpyridine

Weight of Coal Before Extraction	Weight of Coal After Extraction	Wt% Loss of Dry Coal
6.0559 g	1.352 g	22.3
7.0325 g	1.807 g	25.7
6.5531 g	1.645 g	25.1
Average Weight Loss	Standard Deviation.	
24.367	1.81 %	

2.   Supercritical Fluid Extraction

a.   Factors Affecting Extraction Efficiency and Their Contributions. It has been suggested that the desorption of analytes from environmental matrices requires overcoming the energy barrier of desorption, which could be accomplished by using selective fluids or elevated pressures. Increasing the extraction temperature could also be effective. Changing the temperature of an extraction has been used to enhance extraction efficiencies and class-fractionation capabilities for processing applications.[21, 22]

The addition of organic modifiers (e.g., methanol) to supercritical CO_2 has been shown to dramatically increase extraction efficiencies[23-25] of some organic compounds. However, since the mechanisms that control SFE of environmental samples are poorly understood, choosing a modifier for a particular application can be difficult. The use of modifiers can also complicate the analysis of the extracts since the extracts will contain high concentrations of the modifier which may (for example) degrade chromatographic performance or directly interfere with the detection of target analytes (e.g., total petroleum hydrocarbon determinations using infrared detection).

The following experiments were devised to study the effects of various factors on the extraction efficiency. The coupled static/dynamic mode was used for these experiments. In each experiment, a static extraction was performed followed by an one-hour dynamic extraction. The time for the static extraction was one of the factors that is being studied. Methanol was chosen as the modifier for some of these experiments while in other experiments only pure CO_2 was used.

Temperature and pressure were the other two factors being considered. Since the solvent strength of a supercritical fluid is believed to be directly related to its density,[26] there could be interaction between temperature and pressure. The factors are represented in the following table.

Table 9.   Factors and Levels for SFE

FACTORS	FIRST LEVEL 1	SECOND LEVEL 2
Temperature	T1 = 60	T2 = 110
Pressure	P1 = 2000	P2 = 6000
Static Time	t1 = 15	t2 = 60
Modifier	M1 = pure CO2	M2 = CO2 + MeOH
Interaction between Temperature and Pressure	(T×P)1= T1 and P1 or T2 and P2	(T×P)2 = T1 and P2 or T2 and P1
Interaction between Temperature and Modifier	(T×M)1 = T1 and M1 or T2 and M2	(T×M)2 = T1 and M2 or T2 and M1

The orthogonal array $L_8(2^7)$ was chosen to arrange these experiments, and the conditions for each experiment was shown as the following table.[27]

Table 10. Orthogonal Array L_8

T	M	T×M	P	T×P	t	e	
1	1	1	1	1	1	1	1
2	1	1	1	2	2	2	2
3	1	2	2	1	1	2	2
4	1	2	2	2	2	1	1
5	2	1	2	1	2	1	2
6	2	1	2	2	1	2	1
7	2	2	1	1	2	2	1
8	2	2	1	2	1	1	2

Table 11. Assignment by Orthogonal Array L_8 and Experimental Data

No.	T (°C)	Method	P (psi)	t (min)	Weitht loss (%)
1	60	pure CO_2	2000	15	0.27
2	60	pure CO_2	6000	60	0.40
3	60	CO_2+MeOH	2000	60	0.25
4	60	CO_2+MeOH	6000	15	0.27
5	110	CO_2	2000	15	0.47
6	110	CO_2	6000	60	0.55
7	110	CO_2+MeOH	2000	60	0.35
8	110	CO_2+MeOH	6000	15	0.47

To obtain the respective variations, a supplementary table was constructed as follows:

Table 12. Supplementary Table

Factor and Level	Total by Level	Factor and Level	Total by Level
T1	1.17	(T×M)1	1.49
T2	1.84	(T×M)2	1.54
M1	1.69	(T×P)1	1.54
M2	1.34	(T×P)2	1.49
P1	1.34	Col. 7, 1	1.44
P2	1.69	2	1.59
t1	1.48		
t2	1.55	Total	3.03

The respective variations are obtained as follows.

$$CF = 2.9^2/8 = 1.05 \qquad\qquad f = 1$$

$$S_{total} = 0.27^2 + 0.4^2 + 0.25^2 + 0.27^2 + 0.47^2 + 0\ 55^2 + 0.25^2 + 0.47^2 - CF$$

$$= 0.087$$

$$S_T = (T_1 - T_2)^2 / 8 = (1.17 - 1.84)^2/8 = 0.053 \qquad (f = 1)$$

By proceeding similarly, we find S_M, S_P, ..., Se.

$S_M =$	0.015	(f = 1)
$S_P =$	0.015	(f = 1)
$S_t =$	0.00061	(f = 1)
$S_{TM} =$	0.00031	(f = 1)
$S_{TP} =$	0.00031	(f = 1)
$S_e = SCol.7 =$	0.0028	(f = 1)

$$F_A = V_A/V_e = 0.053 /0.001 = 53$$

$$F_B = \qquad\qquad 15$$

$$F_C = \qquad\qquad 15$$

We therefore obtain the analysis of variance as is shown in Table 13.

Since the number of degrees of freedom of e is small, we pool the sources of small variances to form the error variance, and test for significance against this. We estimate the sources found to be significant.

Table 13. Analysis of Variance Table

Source	Degrees of freedom f	Variance S	Variance V	Variance ratio F_o
T	1	0.053	0.053	53**
M	1	0.015	0.015	15*
P	1	0.015	0.015	15*
t	1	0.00061	0.00061O	
TM	1	0.00031	0.00031O	
TP	1	0.00031	0.00031O	
e	1	0.0028	0.0028 O	
e'	(4)	(0.004)	0.001	

(O symbols pooled)

In the F-table for 1 degree of freedom in the numerator and 4 degrees of freedom in the denominator, the value for 5% is 7.71 while for 1% is 21.20. So, T is significant at 1%, M and P are significant at 5%, while TM, TP and t are not significant compared with error. Temperature is the most important factor here.

From Table 10 we can see that the higher the temperature the larger the weight loss. Pressure also affects the weight loss a lot - the higher the pressure the larger the weight loss.

The use of a modifier is another important factor; however, when methanol was added, the weight loss decreased, which is opposed to the idea that when a certain modifier

is added to the system the extraction efficiency should increase. The reason may be that

methanol is not a good modifier for this kind of system and at a temperature below 110°C

the methanol interacts with the sample and can not desorb completely after extraction. To

prove it, another experiment was performed as follows.

Table 14. Working Conditions and the Results
(T = 145°C, P = 9000 psi, t= 30 minutes for stabilization)

Condition	Weight Loss (%)	Average
Pure CO_2	0.71	
	0.78	0.74
CO_2 + MeOH	1.09	
	1.08	1.08

It is clear that at a higher temperature and pressure, the weight loss when MeOH was

added was larger than when pure CO_2 was used.

b.   Further Studies on the Effect of Conditions on the Weight Loss. As seen from

the results above, the higher the temperature and the pressure, the larger the weight loss. The

effect of temperature on weight loss is more significant than pressure, which is in agreement

with the results by Langenfeld[28] - temperature is more important than pressure for achieving

high extraction efficiencies when the interactions between pollutant molecules and sample

matrices are strong. The largest weight loss, when T = 145°C, P = 9000 psi, and methanol was used as a modifier, was only 1.09. This value was much smaller than when the soxhlet method was used, which indicates that the interactions between organic molecules and coal matrixes were too strong to extract by CO_2 even when methanol was used as the modifier. In the following experiments, different methods were used to break the interactions before or during the extraction to determine whether the weight loss can be increased. The results are shown in Table 15. The maximum weight loss here was 1.4 when the sample was preheated at 350°C for half an hour. Preheating at a high temperature could break some large molecules into smaller ones, or reduce interactions between some of the organics and the matrix.

CH_2Cl_2 is the best modifier here, probably because it desorbed easier than others. Pretreatment with HCl also has some effect on the weight loss, indicating that HCl did dissolve some of the inorganic salts on the surface of the coal, leaving some of the organics to be easily extracted. In general, pretreatment or using some modifiers to break the interactions between organics and the coal matrix did increase the weight loss; however, none of the results here can be comparable with the Soxhlet extraction.

Table 15. Different Working Conditions and Their Weight Loss

Number	Condition	Modifier	Weight Loss (%)
1	T=140°C, P=6500psi t=40 min		0.83
2	T=105°C, P=7000psi t=30 min	0.05 mL CH_2Cl_2	1.2
3	T=70°C, P=7000psi t=30 min	0.1 mL toluene	0.9
4	350°C preheated For half an hour P=6500psi,T=140°C t=40 min		1.4
5	T=60°C, P=6500psi t=70min+30min	2 mL benzene	0.2
6	T=120°C,P=7000psi t=6 hrs	2 mL methanol	0.4
7	T=130°C P=7000psi 2+1 hrs	2 ml 2-methyl- pyridine	-0.4

--- Continued ---

Table 15. Continued

Number	Condition	Modifier	Weight Loss (%)
8	stirred and heated in 1N HCl for half an hour, washed and dried. T=130°C, P=7000psi, t=2 hrs		1

IV. CONCLUSIONS

A. For determination of inorganic compositions in coal ash by glow discharge-atomic emission spectroscopy(GD-AES).

(1) Graphite can be used as a host material to make the pellets of the ash. When 90% graphite was mixed with 10% ash, the pellets had good conductivity and mechanical strength suitable for analysis by GD-AES.

(2) The preburn process is very important to the success of analysis. Conditions of 20 mA and 700 v preburning for 2 minutes is good enough for subsequent analysis to get stable signals.

(3) The power of the lamp affects the emissions greatly. The higher the current or the voltage, the larger the intensities of the emissions.

(4) The weight percent of Al, Ca, Fe, Mg, Mn, P, Si and Ti in coal ash can be analyzed silmutanuously by GD-AES. Most of these elements have linear calibration curves when graphite is used as the host material.

(5) When copper was used as the host material, the intensities of the emission signals by all the elements are much larger than those produced by graphite.

(6)   The higher the voltage the shorter time it takes for the emission signals to become stable; however, high voltages can cause erratic discharge, or even halt the process.

(7)   Copper is more promising as the host material.

B.   For the study of coal extratability by supercritical fluid extraction:

(1)   Temperature is the most important factor for extraction efficiency. Pressure and modifiers are also important factors.

(2)   Some of the ways to break the bonds between the extractable compounds and the coal matrix before or during extraction did increase the efficiency greatly. However none of the ways tried proved to be as efficient as the soxhlet extraction.

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