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Optimization of Coal Trace Metal Analysis
By Graphite Furnace Atomic Absorption
Spectrometry

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N.L. Mackintosh
1B Applied Chemistry
7 September 1992

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OPTIMIZATION OF COAL TRACE METAL ANALYSIS
BY
GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

Energy, Mines and Resources Canada
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7 September 1992

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Mr. J.C. Wilson, Director
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Dear Sir:

This report entitled "Optimization of Coal Trace Metal Analysis by Graphite Furnace Atomic Absorption Spectrometry", was prepared as my 1B Work Report for the Surface Science Hydrocarbon Characterization Group - Energy Research Laboratories of Energy, Mines and Resources Canada. This is my first work term report.

The Energy Research Laboratories, having the most advanced analytical and chemical characterization facilities in Canada, develops technologies for efficient use of hydrocarbon fuels and energy.

The Surface Science Hydrocarbon Characterization Group is headed by Dr. Jean-Pierre Charland and is primarily involved with the development of new analytical methodologies for characterizing fossil fuels. This report explains the developed method of analysis of trace metals in coals used by Energy, Mines and Resources.

This report has been prepared and written by me and has not received any previous academic credit at this or any other institution. I would like to thank Mr. Robert Dureau and Mr. Louis Yanke for their assistance in preparing this document.

Sincerely,

N.L. Mackintosh

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SUMMARY

This report deals with the optimization of a method to determine trace metals in coals by graphite furnace atomic absorption spectrometry.

A description of the instrumental parameters optimized, the sample preparation methods utilized and common difficulties encountered are given. The results of the commissioning and testing are shown, conclusions drawn and recommendations made.

It was concluded that a proper temperature program was critical for accurate analysis, and although the fusion sample preparation method was faster, it was not as effective as the acid digestion method. Despite contamination problems with zinc, this technique was sufficient to adopt it as a permanent method for the analysis of coals and coal residues at the Energy Research Laboratories (ERL).

It is recommended that a proper drying temperature of 160°C be used, that the first three firings be monitored visually and audibly, and that the necessity of analyzing zinc be reviewed.

CONCLUSIONS

The aim of this study was to find a suitable method for sample preparation as well as to optimize instrumental parameters and working conditions for the determination of 12 elements commonly found in coals. The best sample preparation method for each element has been determined along with the optimum instrumental conditions.

The method gives accurate results for all the elements except zinc. For most of the elements contamination was not a factor affecting accuracy. For other elements, however, care must be taken during preparation. The accuracy of the zinc results recorded by the attempted methods within this phase were very poor.

Although a drying temperature of 140°C was in most cases effective, there were some elements which, due to the condition of the cuvette, required a drying temperature of 160°C. The drying program will vary, according to the element analyzed previously and the number of firings on the graphite cuvette.

In order to minimize the memory effects, a sufficient atomizing temperature was required. For some elements it was necessary to use the maximum temperature of 3000°C. It was crucial to ensure the sample absorbance returned to the baseline before entering the cleaning stage. The atomizing temperature will differ, depending on the concentration of the element in the sample being analyzed.

Although the slow fusion sample preparation method was faster, easier and safer it did not prove as effective as the acid digestion preparation method.

Using nickel nitrate, in a concentration of 2000 ppm, as a matrix modifier for Arsenic gave excellent results.

Realistic linear curve ranges were determined.

The flux in the fusion samples created a more complicated matrix and thus more interference. This was compensated for by altering the temperature programs.

RECOMMENDATIONS

Because of the poor accuracy of the zinc results recorded by all methods, the need to analyze zinc should be reviewed in the next phase of the project.

In addition, the next phase should include experimentation with the autosampler and its capabilities, particularly the creation of standards and additions of matrix modifiers.

To ensure proper drying of a sample it should be monitored visually and if necessary the temperature should be increased to 160°C.

1.0 INTRODUCTION

The Surface Science Hydrocarbon Characterization (SSHCC) section of Energy, Mines and Resources Canada (EMR) has proposed a new method for determining trace metals in coals and coal residues. The data generated will allow industrial clients, principally power generating stations and steel factories, to minimize operational problems within boilers, while protecting the environment. An understanding of the transformation of mineral matter in coal, particularly arsenic, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, silver, vanadium and zinc, at high temperatures is essential to acquire the ability to predict the erosion rates of boilers (1). Specific characteristics and qualities are required to rank coal for usage and disposal.

In the past, methodologies used were developed for the analysis of samples with high detection limits, generally major and minor elements. However, with the increase in environmental awareness, it has become necessary to perfect the analysis of samples with very low detection limits, namely, trace and ultra-trace elements, which would otherwise go undetected by inductively coupled plasma (ICP) analyses. Furthermore, a minimum of 5-10 mL of sample is necessary for ICP analyses.

This study was initiated to indicate which sample preparation method, acid digestion or fusion, would maximize sensitivity and accuracy for each of 12 metallic elements. Once it was determined which method was preferable for each element it was necessary to optimize the instrumental method used to analyze each of the elements. An analysis of coal samples later will provide industry with an early detection system for both operational problems and detrimental effects to the environment.

This phase of the study ascertained the specific sample preparation and instrumental method to be used for the eventual analysis of samples.

2.0 EXPERIMENTAL PROCEDURE

2.1 Instrumentation and Materials

The study was conducted using a Hitachi® Polarized Zeeman Atomic Absorption Spectrophotometer, model Z-8270, equipped with a SSC-300 autosampler. Pyrolytically coated graphite tubes (Hitachi Part No. P91 031) were employed.

All the standard solutions were prepared from 1000 ppm stock solutions provided by Delta Scientific Ltd. (Ag, As, Cd, Cr, Cu, Pb, Ni, V) and Plasma-Chem Associates, Inc (Co, Mn, Mo, Zn). All the stock solutions were in 2% nitric acid except for Mo which was in 5% hydrochloric acid.

Concentrated nitric acid (69.0-71.0%) from Baker was used in the preparation of all standard and blank solutions.

Concentrated hydrochloric acid (36.5-38.0%) from Baker and concentrated hydrofluoric acid (40%) from EM Science were used in the preparation of acid digestion samples.

Fusion flux (50% lithium tetraborate, 50% lithium metaborate) was used in the preparation of slow fusion samples.

The deionized water used in the preparation of all standards and samples was of 18 megohm purity.

2.2 Atomic Absorption

Atomic absorption is the process that occurs when a ground state atom absorbs energy in the form of light of a specific wavelength (resonant wavelength) and is elevated to an excited state. The amount of light energy absorbed at this wavelength will increase as the number of atoms of the selected element in the light path increases. The relationship between the amount of light absorbed and the concentration of analyte present in known standards can be used to determine unknown concentrations by measuring the amount of light they absorb (2).

2.3 Acid Digestion

2.3.1 Preparation of Standards

The acid digestion working standards were prepared by transferring 1.0 mL of 1000 ppm analyte stock to a 100 mL Nalgene volumetric flask. Then 1.0 mL of nitric acid was added and the flask was brought to volume with distilled water. This new 10 ppm working standard was used to create a 1 ppm working standard by the same method, and for Cd, Mn and Mo a 0.1 ppm working standard was made using the 1 ppm standard.

These working standards were then used to prepare the calibration standards. Depending on the linear range of the calibration curve, small volumes ranging from 0.02 mL to 3.0 mL of working standard were added to 10 mL glass volumetric flasks. Nitric acid was added to these flasks (0.1 mL) to raise the acid concentration to 1%. The reason acid was added to the standards was that when left in a neutral solution most elements, especially Cd and Zn, produce hydroxide precipitates or are adsorbed on the container wall. As a result, the concentration of the standard solution lowers with time. If a calibration curve were traced in this condition and measurements of an unknown sample were carried out, its concentration would be higher than the true value. Therefore, to prevent concentrations from being varied, the standards had 0.1 mL of nitric acid, the same acid in the stock solution, added to bring the solution to a concentration of 1%. Each flask was then filled to mark with distilled water.

Preparation of arsenic standards can be found in Section 3.3.1 Matrix Modifiers.

Table II gives the linear curve range for each of the 12 elements.

2.3.2 Preparation of Samples

The coal samples were ashed at 550°C for 6 h to remove any remaining carbon. The resulting ash was subjected to the following digestion. Approximately 0.2 g of the well blended, minus 200 mesh ash was weighed into a 100 mL teflon beaker. Twenty millilitres of trace metal grade aqua-regia (HCl to HNO₃ in a ratio of 3:1) and 20 mL of hydrofluoric acid were added to the sample. The beaker was placed on a hot plate at 130-150°C and heated until dry. When the solution evaporated, the beaker walls were rinsed with deionized water and the sample was heated to dryness a second time. It was then removed from the hot plate and cooled. After it cooled, 1 mL of nitric acid and 5 mL of deionized water were heated in the beaker at approximately 70°C to redissolve the sample. An additional 30 mL of deionized water was added and the sample was heated for approximately 30 min to redissolve the residue. When the final solution cooled it was immediately transferred to a 100 mL polyethylene volumetric flask and diluted to volume with deionized water.

2.3.3 Background Interference

Background interference was minimized using the acid digestion method because of the simple matrices involved. The term matrix refers to everything that is in the sample other than the element being analyzed. All the standards were made from pure, single element stock, therefore eliminating interferences from other elements.

2.4 Slow Fusion

2.4.1 Preparation of Standards

The fusion working standards were prepared by the same method as the acid digestion working standards. That is, 1.0 mL of 1000 ppm analyte stock was transferred to a 100 mL Nalgene volumetric flask, with 1.0 mL of nitric acid. The flask was filled with deionized water, thus creating a 10 ppm working standard. A 1 ppm working standard was created following the same method, only using 10 mL of the 10 ppm standard, rather than 1 mL of the 1000 ppm standard. For Cd, Mn, and Mo it was necessary to make a 0.1 ppm working standard using 10 mL of the 1 ppm standard.

In order to calibrate in the presence of chemical interference, namely, fusion flux, it is important to synthetically match, as closely as possible, the matrix of the standards to that of the samples. For this reason, 2.0 mL of 20 000 ppm flux was added to each of the calibration standards to match the 4000 ppm flux concentration in the samples.

Depending on the linear curve range of the calibration curve, between 0.02 mL and 3.0 mL of working standard was added to 10 mL glass volumetric flasks, each containing 2.0 mL of flux. Nitric acid (0.5 mL) was added to bring the acid concentration to 5%. This again demonstrates the synthetic matrix matching as all the fusion samples are in 5% nitric acid. Each flask was then filled to volume with deionized water.

Preparation of arsenic standards can be found in Section 3.3.1 Matrix Modifiers. The only difference is that 2.0 mL of 20 000 ppm flux is added to each standard before bringing the flask to volume with deionized water.

Table III contains the linear curve ranges for each of the 12 elements.

2.4.2 Preparation of Samples

Three coal samples were prepared by fusion: 1633a, BCR38 and MRG-1. Approximately 0.2 g of each sample was weighed into platinum crucibles. Before using, each crucible was cleaned in a beaker of hot nitric acid for 30 min. Approximately 0.4 g of fusion flux was added to each crucible. The resulting mixture was blended manually for 5 min before being placed in a Fisher Isotemp Programmable Ashing Furnace. The samples underwent a very gradual heating. The temperature within the furnace was raised 1°C/min until it reached 300°C, where it was held for 30 min. The furnace then continued heating at a rate of 1°C/min to 550°C, where it was again held for 30 min. The final ramp of 1°C/min brought the samples to a maximum temperature of 850°C. The coals remained at 850°C for 240 min before being cooled at 10°C/min to a final temperature of 40°C. Once the samples had reached approximately room temperature, they were fused another 20 min in a Thermolyne furnace at 1050°C. The crucibles were then cooled to room temperature. The solid chips of sample in the bottom of each crucible were heated and dissolved in a beaker of 5% nitric acid. It took almost 25 min for each sample to dissolve. When the final solution had cooled, it was transferred to a 100 mL Nalgene volumetric flask and filled to mark with deionized water.

2.4.3 Background Interference

Background interference was noticeable with the fusion samples because the fusion flux created a more complex matrix. The argon gas flow of 30 mL/min greatly decreased the interference.

2.5 Calculations

2.5.1 Acid Additions

The volume (mL) of nitric acid added to the samples was calculated using the following equation:

$$(required\ percentage - actual\ percentage) / 100$$

where required percentage = the consistent percentage at which all standards were to be run, 1% for acids and 5% for fusions.

actual percentage = the current value of acid present after dilution.

2.5.2 Flux Additions

The flux added was in 20 000 ppm solution, therefore the addition was calculated using the equation below:

$$20\ 000\ ppm\ (X\ mL) = 4000\ ppm\ (10\ mL)$$

$$X = 2.0\ mL$$

2.5.3 Dilution Factors

The dilution factors (DF) were calculated using the following equation:

$$DF = [(ppm\ coal\ ash)(weight)] / [(ppm\ solution)(100\ mL)]$$

where ppm coal ash = certified concentration reference value for a particular element in a specified coal ash.

weight = weight of the sample used during initial preparation.

ppm solution = any concentration value which falls within the linear range of the calibration curve, normally the midpoint.

2.5.4 Ratio Correction Factors

The ratio correction factor (RCF) is defined by the following equation:

$$RCF = \text{reference value} / \text{actual value}$$

where reference value = the certified reference value for that particular element and sample.

actual value = the actual value observed by experimentation.

3.0 RESULTS AND DISCUSSION

3.1 Common Difficulties

Several problems repeatedly surfaced. Although in most cases the problem was easily rectified, it was not always possible for quick recognition of the error. Table I provides a list of possible problems one might encounter with their solutions.

3.2 Contamination

The graphite furnace atomizing method is selected for measurements of samples in very small volumes at high sensitivities, therefore allowing measuring errors to occur due to various factors such as atmosphere in laboratories, handling of samples and measuring procedures. To help minimize contamination, a special fumehood was designed which could be lowered over the furnace during analysis. During its installation, the graphite furnace was covered in thick sheets of plastic to prevent contamination. Manganese was run immediately afterward and with a curve coefficient of 0.9997, it demonstrated that the plastic had been effective in preventing dust and ceiling tile particles from falling into the furnace.

With the exception of zinc, it was not necessary to take any particular cautions regarding contamination. All glassware was rinsed in deionized water and fresh standards were prepared each day. Nitric acid was not stored in the beaker, within the fumehood, for more than two days. To reduce contamination of the cuvette caused by diffusion of the vapourized sample, the argon gas flow during atomization was 30 mL/min.

Concerning zinc, the graphite furnace has been termed "the instrument that suffers from hay fever" because of the high probability of gross contamination by particles in the atmosphere (5). Unaware of this information when zinc was originally analyzed the source of contamination was not immediately known. Below is a list of all contamination sources considered possible at the time.

- (1) deionized water
- (2) nitric acid
- (3) pipettes
- (4) volumetric flasks
- (5) sample cup
- (6) graphite cuvette
- (7) plastic containers
- (8) atmosphere

Each source was examined individually. Both deionized water and nitric acid were ran as blanks. Their absorbance was very close to zero (0.001 abs) and it proved the water and acid were not the source of contamination.

The next step was to eliminate error from the pipette tips, which were stored in a large plastic bag and not individually wrapped. Before being used, each pipette tip was rinsed with nitric acid. Still, the values did not stabilize.

Although all the plastic flasks and beakers were Nalgene, there was a possibility that they were the source of contamination. New glass volumetric flasks and beakers were washed in nitric acid and then rinsed in deionized water before using. The plastic autosampler cups were filled with deionized water and soaked for 24 h. Zinc was run again with poor results.

The cuvette was relatively new (less than 100 firings) yet it was replaced to ensure it was not the source of contamination.

The only source left was atmosphere. In order to minimize the exposure to the air, all the standards were made in the fumehood. The zinc results did not improve. Purely by accident, the source of contamination was discovered. While trying to ensure the sample was homogeneous, a sample cup was inverted twice, covered by a finger. The peaks and absorbances measured immediately afterwards were enormous. The graphite furnace was so sensitive to zinc that levels found on human skin caused absorbances to rise dramatically. The current status of the laboratory could not provide an environment clean enough to accurately analyze zinc.

3.3 Optimization of Instrumental Parameters

3.3.1 Matrix Modifiers

During the ashing stage it is common to minimize the furnace temperature to prevent the analyte from dispersing. However, if the ashing temperature is not increased for samples with complex matrices significant background will occur at the atomizing stage. This is caused by the sudden increase in temperature, resulting in atomization of the analyte as well as any other remaining organic substances which have yet to be evaporated. Therefore, an additive is introduced to modify the matrix, thus the term matrix modifier. This modifier will alter the chemical compound form in such a way that the analyte element will not disperse even at a higher temperature (3). This fact means the ashing temperature can be raised to remove any organic substances, which could cause interference during atomization, without fear of losing any analyte.

A variety of matrix modifiers are available including nickel nitrate, magnesium nitrate and aluminum nitrate. Both nickel and magnesium are commonly used as modifiers. Because nickel was one of the metals involved in the study, it was decided to use magnesium as a modifier for arsenic. Figure I shows the sensitivity condition in which magnesium nitrate was added to arsenic (analyte element) and the ashing temperature was changed. As can be seen from the plot, while arsenic with no modifier begins to disperse at 450°C, arsenic with magnesium nitrate added does not disperse up to about 1300°C.

The suggested concentration of magnesium is 2000 ppm, which can either be manually added to the standards when prepared or added during analysis by the autosampler. The autosampler normally injects 20 μL of sample into the graphite cuvette, but can be programmed to inject 10 μL of sample and 10 μL of modifier. The difficulty found with this method was that although the computer software allowed one to choose which you would prefer to inject first, the modifier or standard, it is not capable of achieving a homogeneous solution inside the cuvette. This unfortunately minimized the effect of the modifier.

In order to maximize the effect of the modifier, the arsenic standards were prepared by manually adding the magnesium nitrate. This was accomplished by pipetting each of 0.1, 0.2, 0.4, 0.7, 1.0, 1.2 and 1.5 mL of 1 ppm working standard into a 10 mL glass volumetric flask. To bring the acid level in the solution to 1% 0.1 mL of nitric acid was added to the flask. The magnesium was of 10 000 ppm stock so 2.0 mL was added to each of the 10 mL flasks, to bring the modifier concentration to 2000 ppm. Each flask was then filled to mark with deionized water.

This method proved very effective in minimizing the interference with the arsenic measurements. Figure II clearly shows the presence of the modifier during analysis. Ramp 1 is the drying stage (80-140°C) where a large part of the magnesium nitrate (which melts at 95°C) as well as other organic substances are removed. During the ashing stage, at 400°C, more magnesium nitrate is boiled off with organic substances. Finally, during the third ramp, which is the atomizing stage at 2800°C, we can clearly see that any slightly remaining causes of interference are removed and corrected for before the analyte is atomized.

3.3.2 Background Interference

Interferences may be defined as sample related effects that alter the measurement accuracy of the analyte relative to the calibration (4).

The background interference in the fusion samples was much more visible than in the acid digestion samples. Yet, the background was minimized by the argon gas flow at 30 mL/min. This decreased the level of interference because the argon swiftly carried the products of coexisting substances such as molecular vapour and smoke, which cause background absorption, out of the cuvette. Unfortunately, for measurements in a high concentration area, flowing a large amount of gas at the atomizing stage lowered the atomic absorption sensitivity. However, the lower sensitivity did not affect the accuracy of the results. Therefore, all analyses were made with gas on during atomization.

3.3.3 Preparation of Samples

The acid digestion sample preparation method had accurate results for five elements (As, Cd, Cu, Mn and Pb), while the slow fusion method had accurate results for four elements (Cd, Cu, Ni and V). Note that both methods were equally accurate for Cd and Cu.

Because the acid digestions required much more effort during their repeated drying stages and dealt with dangerous acid, namely, hydrofluoric acid, it was preferable to use the fusion method. The drawback was that the samples were in 5% nitric acid solution rather than 1% as were the fusion samples. The increased acid concentration led to a decrease in the life expectancy of the graphite cuvettes. The fusion samples were still preferable however since they were prepared in a day and a half and the acid digestions required three days.

Tables IV and V provide the accuracy of the acid digestion results and fusion results respectively.

3.3.4 Detection Limits

The detection limits were determined by the procedure of analyzing a blank (1% nitric acid) and a minimum of five standards within the expected detection limits. The cases in which the blank and the first standard had very similar absorbances (close to 0) demonstrated that the expected lower limit was in fact too low for detection. The first standard was then increased in concentration by 2 ppb and again analyzed after a blank. This procedure was repeated until the instrument was capable of distinguishing between the blank and the lower limit standard. It was also necessary that the RSD be less than 5% to ensure measurements on the edge of the detection limits were repeatable (6).

The upper limit of detection was easily noted as the point where the instrument could no longer differentiate between standards.

Both Tables II and III contain the optimum detection limits (measurable concentration range) for the 12 elements.

3.3.5 Linear Curve Ranges

It was important to find the linear curve range for each element because accurate measurements are difficult in the high concentration range within which the calibration curve has a large curvature.

After the detection limit of each element was determined it was possible to define the linear curve range for each. This was accomplished by running six standards within the defined detection limits, from which the computer would graph the calibration curve. By visual inspection of the curve, it was noted the points above and below which the curve failed to remain linear. For most of the elements, except Mn, the curve was linear at the lower detection limits and only began to curve at the upper limits. The linear curve ranges for all the elements analyzed are shown in Tables II and III.

3.3.6 Temperature Programs

The temperature program for each element was crucial for accurate and repeatable measurements. Table VI shows the optimum temperature program for each element.

Four distinct stages create each temperature program - drying, ashing, atomizing and cleaning. The drying stage must completely dry the sample to prevent sudden boiling at the ashing and atomizing stages, degrading accuracy and repeatability. Samples that are not effectively dried often burst, making a popping sound, at the beginning of the ashing stage, leaving sample droplets on the furnace lid. An improper drying stage could also be detected on the computer readout. Peaks should appear only in the atomizing stage. An abnormal peak in the drying stage indicates the temperature is too high, while a peak in the ashing stage indicates the drying temperature is too low. Figures III and IV show these abnormal peaks along with their corrections.

The drying stage is the most crucial and difficult stage to optimize. Manganese analysis delayed this study a week due to drying problems. Manganese, which usually produced very accurate results suddenly had RSD's over 20% and inaccurate values. An increase in background was noticed as well as an unfamiliar "popping" sound during the ashing stage. Unaware of the cause all the variables were reset or replaced individually. A new cuvette was installed, the windows and pole ends within the furnace were cleaned and all standards were made fresh. Still the results did not improve. Considering the possibility of an instrumental problem, copper, which normally has very good results, was run. A curve coefficient of 1.0000 was achieved (See Figure V) ruling out the possibility of instrumentation. Manganese was run again after changing the slit width from 0.40 nm to 0.20 nm, but had no effect. The atomizing temperature was increased from 2500°C to 2650°C and still no change occurred.

Attention was then directed to the "popping" noise at the beginning of the ashing stage. The sample was observed within the furnace during the drying stage by a method shown in Figure VI. This observation indicated that the sample was not centred within the cuvette and not drying properly. The drying ramp time was increased from 40 s to 50 s, which was still not enough. The drying temperature was increased to 160°C from 140°C. The "popping" sound ceased and the absorbances stabilized. The need for the increased temperature was explained by the possible formation of manganese nitrate tetrahydrate, which has a melting temperature of 129°C. The pyrolytic coating of the cuvette provided such a smooth surface that the sample slid forward within the tube and did not remain centred. Although the drying temperature was set at 140°C, the actual temperature at the front edge of the cuvette was much less. By increasing the drying temperature to 160°C the sample would dry properly regardless of its position within the tube.

The second stage of the temperature program is called ashing. A sample is ashed to eliminate interference at the atomizing stage. At this stage all organic and inorganic substances with low boiling points will be evaporated. It is important to maximize the ashing temperature to reduce background absorption. However, an ashing temperature which is too high could result in a loss of analyte element. The elements with the most sensitive ashing temperature were Cd, Mn and V. Cadmium should be ashed at only 300°C, vanadium at 600°C, rather than 900°C, to avoid melting nitrates, and Mn at 750°C instead of 500°C to minimize interference.

The atomizing stage follows the ashing stage in a temperature program. Since analytical accuracy is directly dependent on the atomizing temperature, it is necessary for this stage to set up conditions which assure proper atomization of the analyte element. Conditions for the atomizing stage also have a relation with the life of the graphite cuvette. Its deterioration is accelerated by raising the atomizing temperature. Both Cd and Pb required relatively low atomizing temperatures, 1800°C and 2000°C respectively, because of their low melting points. Elements with high boiling points, primarily Cr, Mo and V, required much higher atomizing temperatures, 2900°C, 3000°C and 3000°C respectively. Temperatures lower than this caused memory effect, thus degrading accuracy and repeatability. Memory effect occurs when an incompletely evaporated analyte element remains in the graphite cuvette and affects the next measurement. An example of memory effect (often called tailing) is shown in Figure VII. Note that the absorbance does not return to the baseline.

The final stage is cleaning. After completing the atomizing stage, residue of evaporated sample may adhere to both ends of the cuvette or inside wall. If the next analysis is started in this condition, accuracy is degraded due to contamination. At the cleaning stage the cuvette is heated to a temperature higher than that of the atomizing stage to evaporate and eliminate the adhering matter after completing each measurement. Optimum cleaning temperatures are given in Table VII. Note that all analysis in this study utilized pyrolytic tube type cuvettes.

4.0 REFERENCES

1. Bauer, F., Nayak, R., Tonden, T.
"Mineral Matter in Coal - Origin, Identification, High Temperature Transformation and Boiler Erosion",
Journal of Coal Quality.
April, 1987.
2. Beaty, R.
"Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry".
Perkin-Elmer Corp., U.S.A., 1978.
3. Graphite Atomization Analysis Guide for Polarized Zeeman Atomic Absorption Spectrophotometry.
Hitachi, Japan, 1988.
4. Instruction Manual - Model Z-8200 Series Polarized Zeeman Atomic Absorption Spectrophotometer.
Hitachi, Japan, 1991.
5. Morgenthaler, L.
"A Primer for Flameless Atomization", American Laboratory.
April, 1975.
6. The Guide to Techniques and Applications of Atomic Spectroscopy.
Perkin-Elmer Corp., U.S.A., December, 1983.

Table I - ERROR DISPLAYS AND THEIR SOLUTIONS

Error No.	Display Comment	Cause of Occurrence	Troubleshooting Recovery Method
1.	Increase cooling water flow.	Cooling water volume is less than fixed value.	Check the volume of cooling water.
2.	Light intensity too low, check condition.	Light intensity is less than 20.	If there is anything which interrupts the light path, remove it and check hollow cathode lamp and analytical conditions.
3.	Set cuvette in GA furnace.	No cuvette is installed, or a cuvette is installed incorrectly.	Install a cuvette, or remove and install properly.
4.	Close GA furnace lid.	Measurements were started without shutting the lid of GA oven.	Shut the lid of GA oven and check to ensure lamp is ignited.

Table I - ERROR DISPLAYS AND THEIR SOLUTIONS

Error No. Method	Display Comment	Cause of Occurrence	Troubleshooting Recovery
5.	Ar gas pressure too low.	Ar gas pressure was less than fixed value.	As pressure in Ar tank nears 500 psi, replace it with a new tank.
6.	Reset GA autosampler.	Measurement was stopped during run.	Reset autosampler.
7.	RSD's (relative standard deviation) are above 10.	<ul style="list-style-type: none"> i) destroyed tube ii) poor sample injection iii) non - homogeneous standard or sample iv) wrong lamp in use 	<ul style="list-style-type: none"> i) Replace the tube if any bubbling or flaking is visible. ii) Reposition nozzle on auto-sampler. iii) Shake solutions well for 2 min. iv) Check lamp.

Table II - ACID DIGESTION RESULTS

Element	Measurable Conc. Range (ppb)	Linear Curve Range (ppb)	Light/Temp. Control	COMMENTS re: Temperature program gas on during atomization
Ag	2-200	2-40	ON	1) A low atomizing temp. narrows the range of conc. in which the calibration curve is linear.
As	10-500	10-150	ON	
Cd	0.25-20	0.25-10	OFF	1) Atomize at 1800°C. 2) Ashing temp. should be 300°C.
Co	2-200	2-100	ON	
Cr	10-1000	10-70	ON	
Cu	1-80	1-80	ON	1) Gas off during atomization will improve sensitivity.

Table II - (cont'd)

Element	Sample (0.20 g)	Dilution Factor	Certified Reference Value (ppm)	Observed Value (ppm)	Corrected Value	COMMENTS
Ag	1633a BCR38 MRG-1		NR	NR		
As	1633a BCR38 MRG-1	3 3	150 ± 15 57 ± 2.3 NR	151 52 NR		1) Takes 40 min. for absor- bance to stabilize after ignition of hollow cathode lamp. 2) Use a magnesium modifier.
Cd	1633a BCR38 MRG-1	None	1 ± 0.15 5 ± 0.3 NR	1.15 5.8 NR		1) Keep lamp current down to 3-4 mA due to self reversal.

NR: No result available

*: Indicates the sample which the corrected ratio values are based upon.

Note: Values in parenthesis are not certified, but are given for information only.

Table II - (cont'd)

Element	Sample (0.20 g)	Dilution Factor	Certified Reference Value (ppm)	Observed Value (ppm)	Corrected Value	COMMENTS
Co	1633a	2	48	56	46.7	1) Use a lamp current of 10 mA.
	BCR38	3	64 ± 1.9	85.6	71.5	
	* MRG-1	4	86	103	86	2) Always use a pyrolytic cuvette to minimize tailing.
Cr	1633a	10	202 ± 6	265	235	1) Watch cuvette condition. Cr seems very harsh on the pyrolytic coating.
	* BCR38	10	(211)	238	211	
	MRG-1	10	450	455		
Cu	1633a	10	122 ± 3	110	116	1) Possible to produce curves with determ. coeff. of 1.0000.
	BCR38	10	208 ± 9	176	198	
	* MRG-1	10	135	129	135	

NR: No result available

*: Indicates the sample which the corrected ratio values are based upon.

Note: Values in parenthesis are not certified, but are given for information only.

Table II - (cont'd)

Element	Measurable Conc. Range (ppb)	Linear Curve Range (ppb)	Light/Temp. Control	COMMENTS re: Temperature program gas on during atomization
Mn	0.5-30	1-20	ON	1) Ash at 750°C to minimize interference. 2) Increase drying temp. to 160°C. 3) Increase drying ramp time to 50 s.
Mo	5-200	5-200	ON	1) Atomize at 2900°C. 2) Clean at 3000°C.
Ni	2-80	2-80	ON	
Pb	5-400	5-300	OFF	
V	2-100	2-100	ON	1) Ash at 600°C rather than 900°C to avoid melting nitrates.
Zn	0.1-3.0	Does not exist	OFF	

Table II - (cont'd)

Element	Sample (0.20 g)	Dilution Factor	Certified Reference Value	Observed Value	Corrected Value	COMMENTS
Mn	1633a	50	185 ± 8	188		1) Use a lamp current of 4 mA. 2. "Popping" sound is due to poor drying.
	BCR38	50	567 ± 16	570		
	MRG-1	100	1340	1320		
Mo	1633a	None	(30)	35		1) Very large memory effect.
	BCR38		NR	NR		
	MRG-1		NR	NR		
Ni	1633a	10	131 ± 4	153	133) second	
	BCR38		(230)	NR) order	
	MRG-1	10	195	219	195) curve	

NR: No result available.

*: Indicates the sample which the corrected ratio values are based upon.

Note: Values in parenthesis are not certified, but are given for information only.

Table II - (cont'd)

Element	Sample (0.20 g)	Dilution Factor	Certified Reference Value	Observed Value	Corrected Value	COMMENTS
Pb	1633a	10	75 ± 0.4	65		1) Not a problem to run samples at 5% HNO ₃ if necessary.
	BCR38	10	262	246		
	MRG-1	10	10	11.4		
V	1633a	20	307 ± 6	228	327	1) Badly corrodes pyrolytic coating on cuvette. 2) Very good results with fusion samples.
	BCR38	20	(395)	256	368	
	* MRG-1	20	520	362	520	
Zn	1633a		227 ± 10	NR		1) Very large contamination problem. GFAA is sensitive to 1 or 2 ppt.
	BCR38		688 ± 29	NR		
	MRG-1		190	NR		

NR: No result available.

*: Indicates the sample which the corrected ratio values are based upon.

Note: Values in parenthesis are not certified, but are given for information only.

Table III - FUSION RESULTS

Element	Measurable Conc. Range (ppb)	Linear Curve Range (ppb)	Light/Temp. Control	COMMENTS re: Temperature program gas on during atomization
Ag	2-200	2-40	ON	1) A low atomizing temp. narrows the range of conc. in which the calibration curve is linear.
As	10-500	10-150	ON	
Cd	0.25-20	0.25-10	OFF	1) Atomize at 1800°C. 2) Ashing temp. should be 300°C. 3) Due to flux a higher temp. program can be used: ashing 450°C, atomizing 2200°C, cleaning 3000°C, which will greatly increase sensitivity.
Co	2-200	2-100	ON	
Cr	10-1000	10-70	ON	
Cu	1-80	1-80	ON	1) Gas off during atomization will improve sensitivity.

Table III - (cont'd)

Element	Sample (0.20 g)	Dilution Factor	Certified Reference Value (ppm)	Observed Value (ppm)	Corrected Value	COMMENTS
Ag	1633a BCR38 MRG-1		NR	NR		
As	1633a BCR38 MRG-1	2.5 None	145 ± 15 48 ± 2.3 0.7	60 98 NR		1) Takes 40 min. for absor- bance to stabilize after ignition of hollow cathode lamp. 2) Use a magnesium modifier. 3) Add the modifier directly to the stand- ards rather than using the autosampler. 4) Inconsistent values may be due to a loss of As during fusion.
Cd	1633a BCR38 MRG-1	None None	1 ± 0.15 4.6 ± 0.3 NR	1.2 4.5 NR		3) Keep lamp current down to 3-4 mA due to self reversal.

NR: No result available.

*: Indicates the sample which the corrected ratio values are based upon.

Note: Values in parenthesis are not certified, but are given for information only.

Table III - (cont'd)

Element	Sample (0.20 g)	Dilution Factor	Certified Reference Value (ppm)	Observed Value (ppm)	Corrected Value	COMMENTS
Co	1633a	2	46	52.6	47	1) Use a lamp current of 10 mA. 2) Always use a pyrolytic cuvette to minimize tailing. 3) Possible to produce curves with determ. coeff. of 1.000.
	BCR38	3	54 ± 1.9	76	68	
	* MRG-1	4	86	96	86	
Cr	1633a	10	196 ± 6	253	195	1) Watch cuvette condition. Cr is very harsh on the pyrolytic coating.
	* BCR38	10	(178)	231	178	
	MRG-1	10	450	344		
Cu	1633a	10	183 ± 3	113		1) Possible to produce curves with determ. coeff. of 1.0000.
	BCR38	10	176 ± 9	175		
	MRG-1	10	135	123		

NR: No result available.

*: Indicates the sample which the corrected ratio values are based upon.

Note: Values in parenthesis are not certified, but are given for information only.

Table III - (cont'd)

Element	Measurable Conc. Range (ppb)	Linear Curve Range (ppb)	Light/Temp. Control	COMMENTS re: Temperature program gas on during atomization
Mn	0.5-30	1-20	ON	1) Ash at 750°C to minimize interference. 2) Increase drying temp. to 160°C. 3) Increase drying ramp time to 50 s.
Mo	5-200	5-200	ON	1) Atomize at 2900°C. 2) Clean at 3000°C.
Ni	2-80	2-80	ON	
Pb	5-400	5-300	OFF	
V	2-100	2-100	ON	1) Ash at 600°C rather than 900°C to avoid melting nitrates.
Zn	0.1-3.0	Does not exist	OFF	

Table III - (cont'd)

Element	Sample (0.20 g)	Dilution Factor	Certified Reference Value	Observed Value	Corrected Value	COMMENTS
Mn	1633a	50	179 ± 8	169		1) Use a lamp current of 4 mA. 2. "Popping" sound is due to poor drying.
	BCR38	50	479 ± 16	478		
	MRG-1	100	1340	1127		
Mo	1633a	None	(29)	NR		1) Very large memory effect.
	BCR38		NR	NR		
	MRG-1		NR	NR		
Ni	1633a	10	127 ± 4	123		
	BCR38		(194)	197		
	MRG-1	10	195	132		
Pb	* 1633a	10	72.4 ± 0.4	57.6	72.4	1) Not a problem to run samples at 5% HNO ₃ if necessary.
	BCR38	10	262	194	246	
	MRG-1	10	10	11.3		
V	1633a	20	297 ± 6	322		1) Corrodes pyrolytic coating on cuvette. 2) Very good results with fusion samples.
	BCR38	20	(334)	370		
	MRG-1	20	520	520		
Zn	1633a		220 ± 10	NR		1) Very large contamination problem. GFAA is sen- sitive to 1 or 2 ppt.
	BCR38		581 ± 29	NR		
	MRG-1		190	NR		

NR: No result available

*: Indicates the sample which the corrected ratio values are based upon.

Note: Values in parenthesis are not certified, but are given for information only.

Table IV - ACID DIGESTION ACCURACY

Element	Sample Values Accurate	Sample Values Corrected by Ratio	Sample Values Inconsistent
Ag	did not run any samples for this element		
As	X Mg modifier		
Cd	X		
Co		X	
Cr		X	
Cu	X		
Mn	X		
Mo			X
Ni		X	
Pb	X		
V		X	
Zn			X contamination

Table V - FUSION ACCURACY

Element	Sample Values Accurate	Sample Values Corrected by Ratio	Sample Values Inconsistent
Ag	did not run any samples for this element		
As	X Mg modifier		
Cd	X		
Co		X	
Cr		X	
Cu	X		
Mn	X		
Mo			X
Ni		X	
Pb	X		
V		X	
Zn			X contamination

Table VI - OPTIMUM TEMPERATURE PROGRAMS

Element: As

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	140	40		200
2	Ash	400	400	30		200
3	Atom	2800	2800		10	30
4	Clean	2900	2900		4	200

Element: Cd

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	140	40		200
2	Ash	300	300	30		200
3	Atom	1500	1500		10	30
4	Clean	1800	1800		4	200

Element: Co

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	140	40		200
2	Ash	600	600	30		200
3	Atom	2700	2700		10	30
4	Clean	2800	2800		4	200

Table VI - (cont'd)

Element: Cr

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	140	40		200
2	Ash	700	700	30		200
3	Atom	2900	2900		10	30
4	Clean	3000	3000		4	200

Element: Cu

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	140	40		200
2	Ash	600	600	30		200
3	Atom	2700	2700		10	30
4	Clean	2800	2800		4	200

Element: Mn

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	160	50		200
2	Ash	750	750	30		200
3	Atom	2800	2800		10	30
4	Clean	3000	3000		4	200

Table VI - (cont'd)

Element: Mo

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	140	40		200
2	Ash	1000	1000	30		200
3	Atom	2900	2900		10	30
4	Clean	3000	3000		5	200

Element: Ni (low temperature program)

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	140	40		200
2	Ash	700	700	30		200
3	Atom	2200	2200		10	30
4	Clean	2600	2600		4	200

Element: Ni (high temperature program)

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	140	40		200
2	Ash	700	700	30		200
3	Atom	2900	2900		10	30
4	Clean	3000	3000		4	200

Table VI - (cont'd)

Element: Pb

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	140	40		200
2	Ash	400	400	30		200
3	Atom	2000	2000		10	30
4	Clean	2400	2400		5	200

Element: V

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	140	40		200
2	Ash	600	600	30		200
3	Atom	3000	3000		10	30
4	Clean	3000	3000		5	200

Element: Zn

Stage No.	Stage	Temperature(°C)		Time (s)		Gas Flow (mL/min)
		Start	End	Ramp	Hold	
1	Dry	80	140	40		200
2	Ash	300	300	30		200
3	Atom	2000	2000		10	30
4	Clean	2400	2400		4	200

Table VII - OPTIMUM CLEANING TEMPERATURES

Type of Graphite Cuvette	Atomizing Temperature	Cleaning Temperature
Cup Type	Not exceeding 2300°C	Atomizing temperature + 200°C
	2400°C or higher	2600°C
Tube type or pyrolytic type tube cuvette	Not exceeding 2700°C	Atomizing temperature + 200°C
	2800°C or higher	3000°C

Figure I - ASHING OF ARSENIC WITH MAGNESIUM NITRATE ADDED

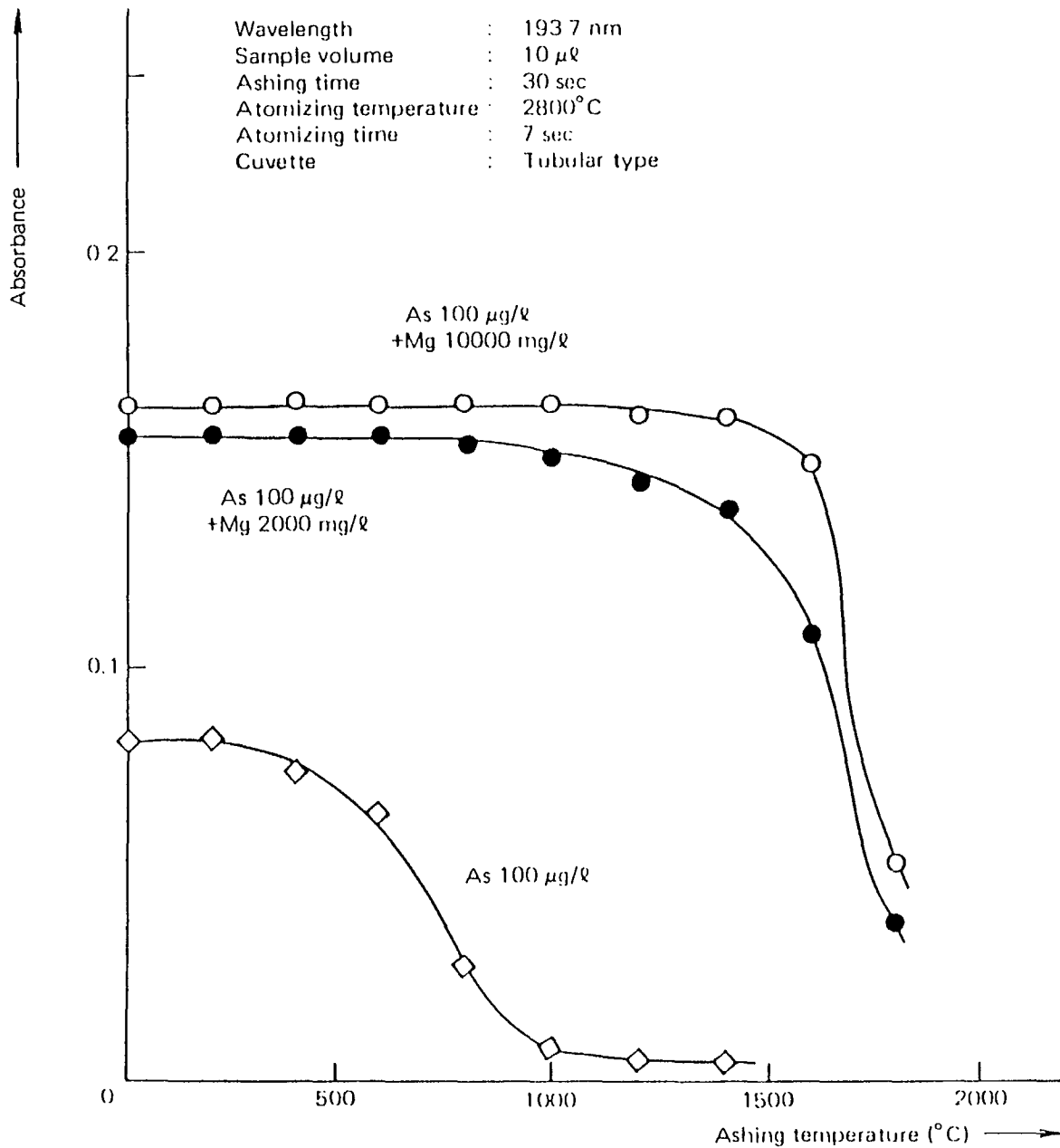


Figure II - COMPUTER READOUT DURING ARSENIC ANALYSIS

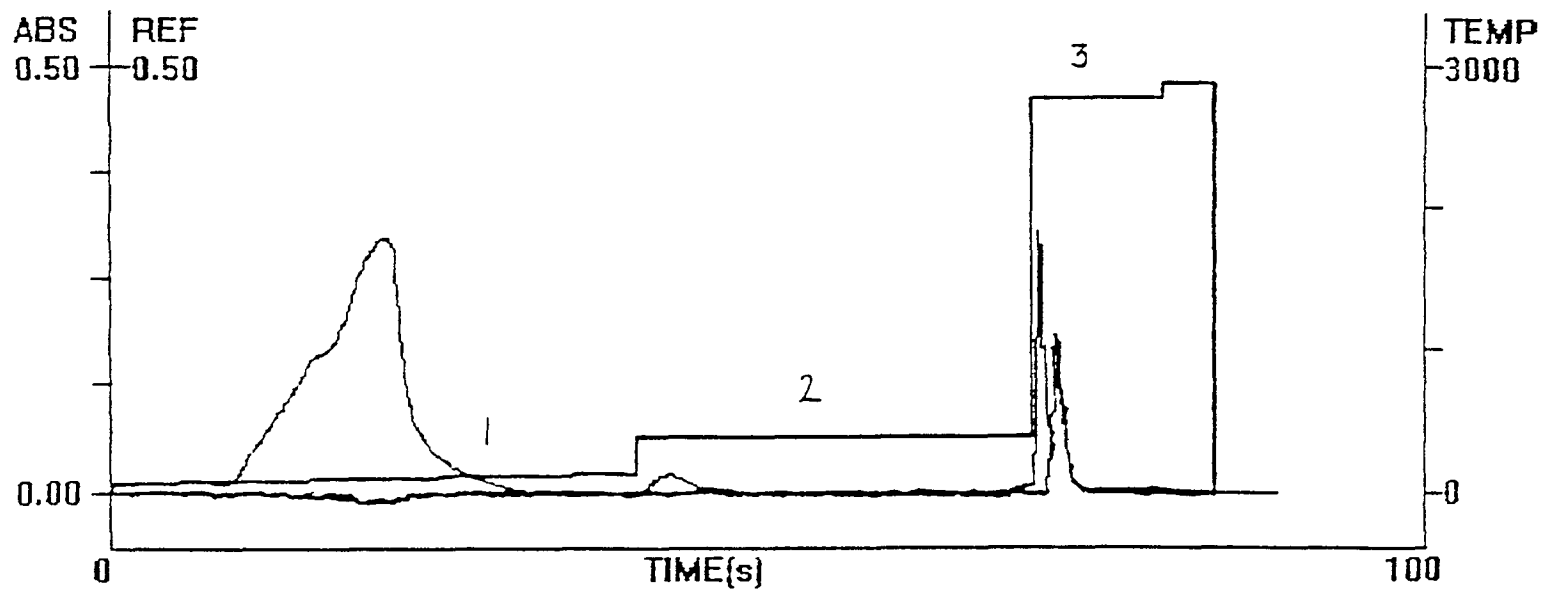


Figure III - EXAMPLE USING TOO HIGH A DRYING TEMPERATURE

Sample : Refreshment drink
(diluted to 1/4 concentration)
Element : Cu
Wavelength : 324.8 nm
Sample volume : 10 μ l
Cuvette : Pyrolytic type tube cuvette
Ashing stage : 600°C STEP mode, 30 sec
Atomizing stage : 2800°C STEP mode, 7 sec

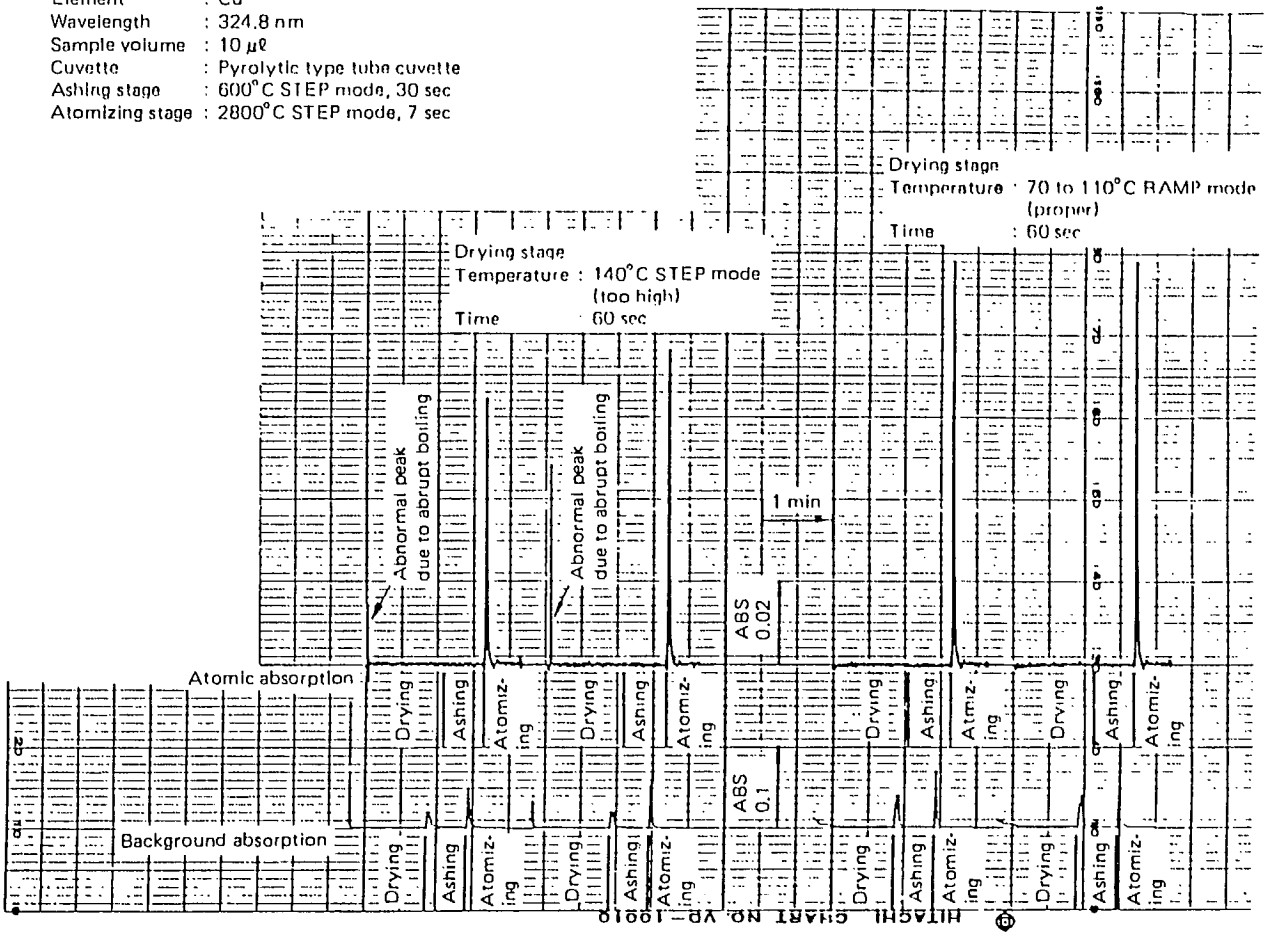


Figure IV - ANALYTICAL EXAMPLE OF INSUFFICIENT DRYING

Sample : Refreshment drink
 (diluted to 1/10 concentration)
 Element : Fe
 Wavelength : 248.3 nm
 Sample volume : 10 μ l
 Cuvette : Pyrolytic type tube cuvette
 Ashing stage : 600°C STEP mode, 30 sec
 Atomizing stage : 2800°C STEP mode, 7 sec

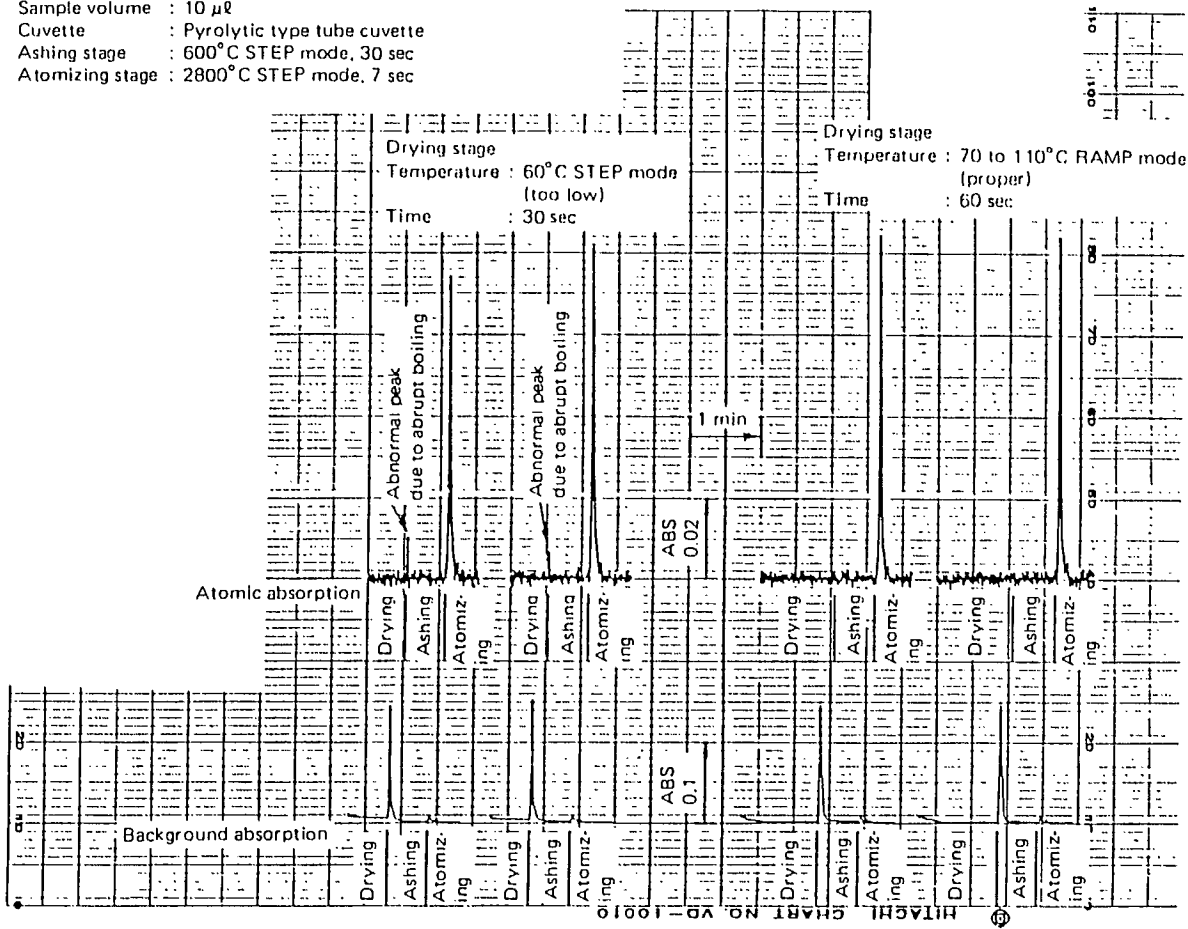


Figure V - COPPER CURVE

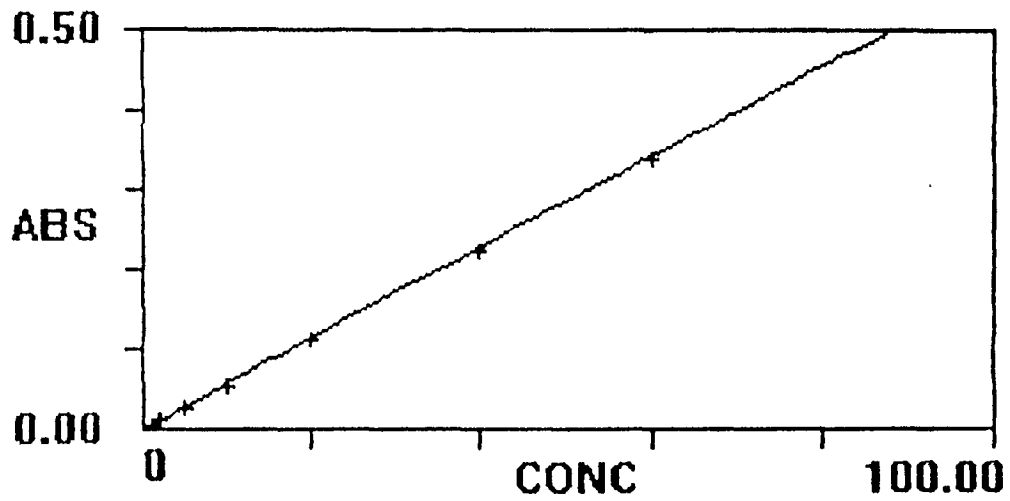


Figure VI - OBSERVATION OF DRYING PROCESS IN CUVETTE

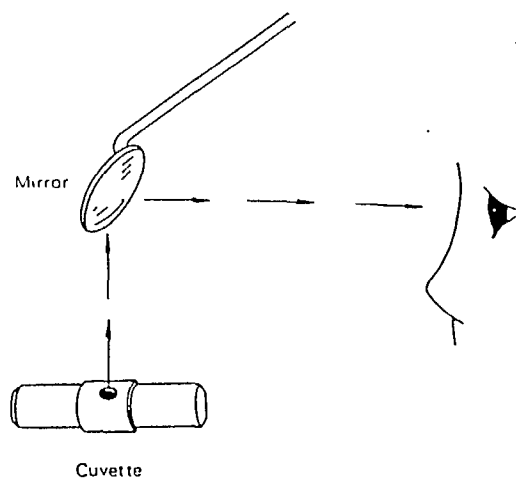


Figure VII - MEMORY EFFECT ON VANADIUM

