



Mobility of boron from coal ash in an aqueous system
by Anne Shirley Halligan

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemistry

Montana State University

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Abstract:

An investigation of boron leachability and adsorption by coal ash under a variety of conditions was undertaken. Boron leachability was studied as a function of pH, time, ash type, particle size, and ash concentration. Total available boron, aluminum, and iron were determined. Ash retention of boron was calculated. The adsorption of boron by ash that was water conditioned and ash that was acid conditioned was studied. A re-leaching of adsorption samples was pursued to determine changes in the ash after adsorption had taken place.

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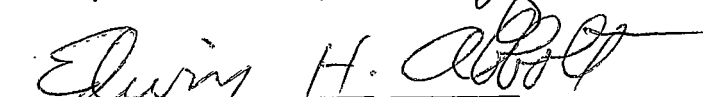
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ABSTRACT

An investigation of boron leachability and adsorption by coal ash under a variety of conditions was undertaken. Boron leachability was studied as a function of pH, time, ash type, particle size, and ash concentration. Total available boron, aluminum, and iron were determined. Ash retention of boron was calculated. The adsorption of boron by ash that was water conditioned and ash that was acid conditioned was studied. A releaching of adsorption samples was pursued to determine changes in the ash after adsorption had taken place.

INTRODUCTION

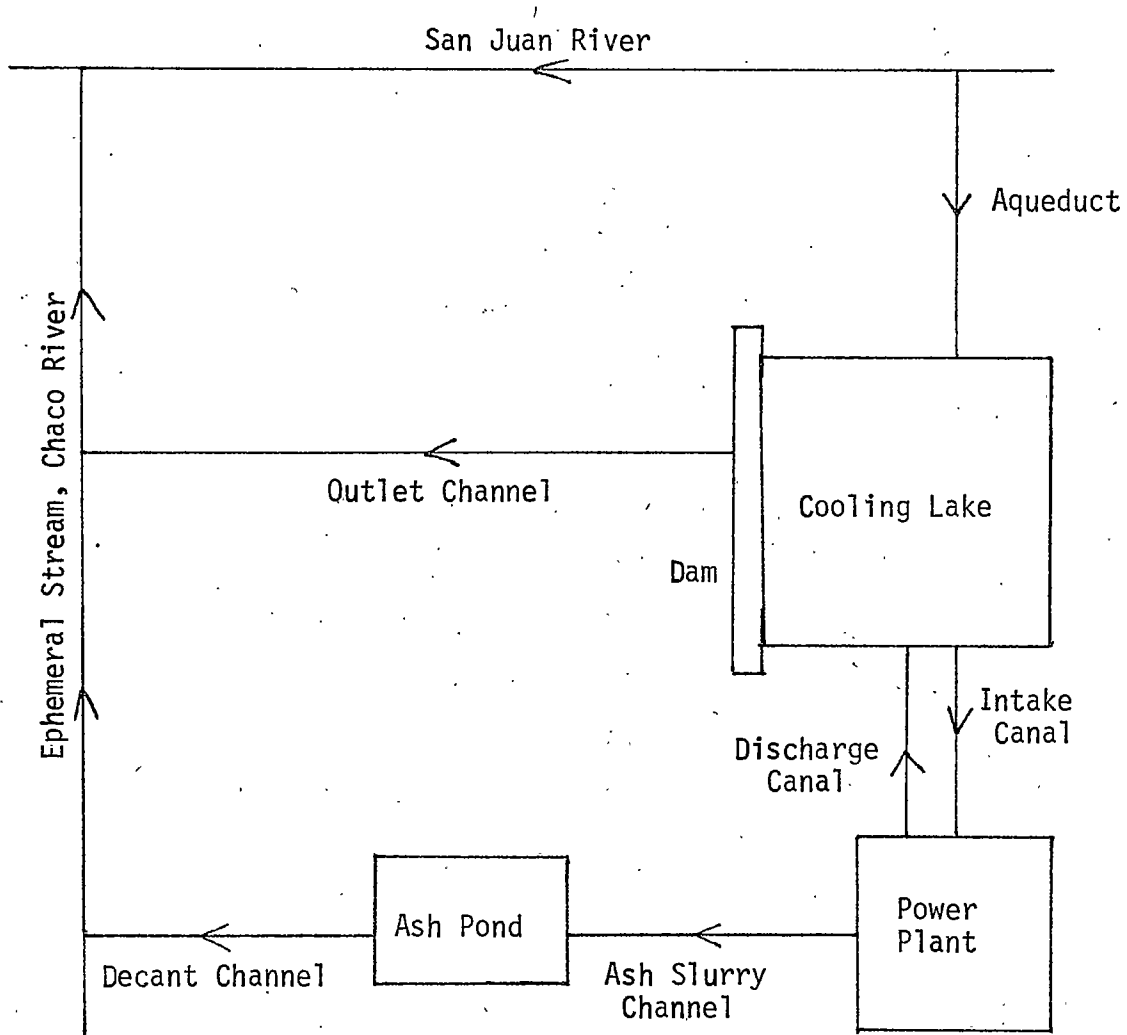
The combustion of coal as a fuel has become an important alternative power source in our modern society. Coal is among the fossil fuels which are readily available, convenient, and practical for use.

Coal combustion, like all other large scale industrial processes, does not come without its technical and environmental considerations. As a mined resource, coal has natural variability in its composition and its properties. For instance, not all coals burn consistently hot depending on when and where they were mined. The solid and gaseous wastes resulting from coal combustion present an increasing challenge in their disposal.

Solid coal wastes are commonly referred to as ash. Several methods of ash disposal are currently in use. One popular method involves sluicing in lagoons. In developing our understanding of the aqueous behavior of a sluicing pond, it is helpful to envision a schematic of a power plant operation. Figure 1 is a schematic originated by Dreesen (1) and it represents water flow at a power plant. The coal is burned in the plant to heat water to produce steam which drives the generators and produces electricity. The function of the cooling pond is to allow the superheated water to cool before returning to the river. The ash pond is involved in an entirely segregated cycle of water. Water is sprayed into the stacks. This procedure cleans the ash out of the stacks and keeps large amounts of particulate matter

Figure 1

Schematic of Water Flow at a Power Plant.
Dreesen and coworkers (1).



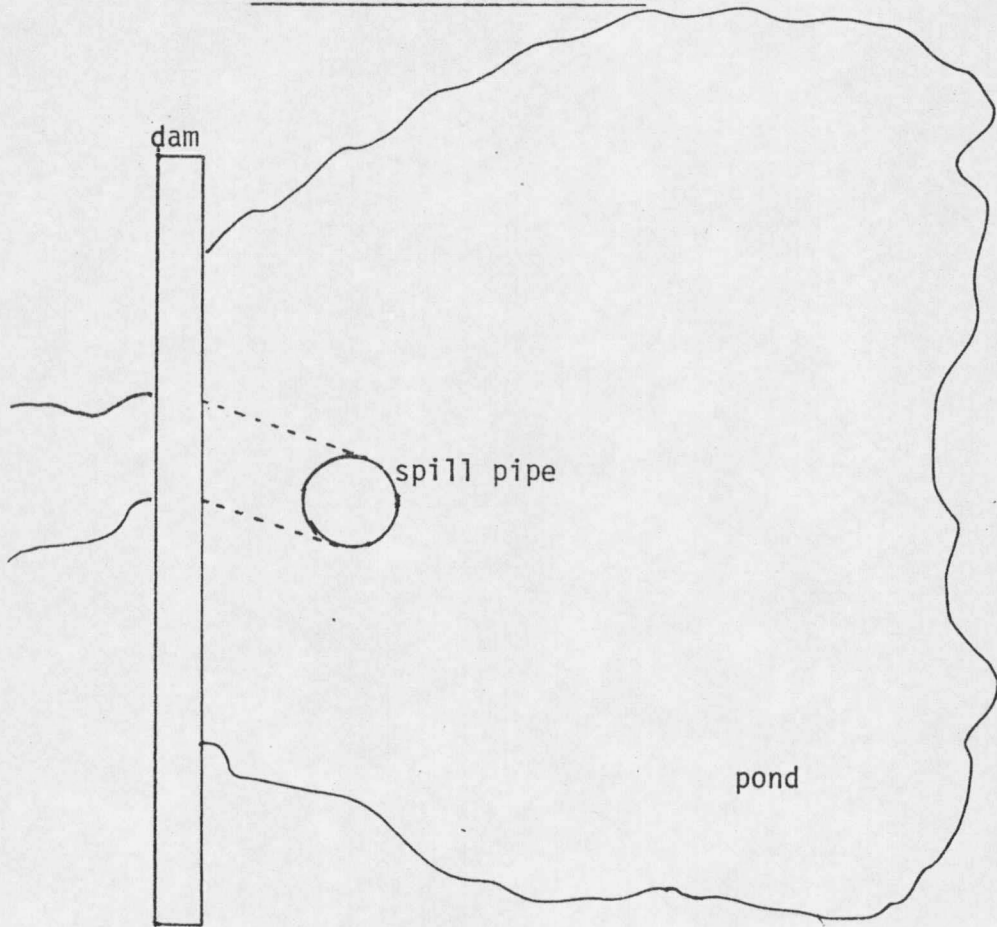
from escaping out of the stacks into the atmosphere and increasing air pollution. The slurry of water and ash is then channeled into the ash pond. The engineering of this pond is schematically shown in Figure 2. During the holding time in this pond, the solid particles in the slurry settle to the bottom and the aqueous portion is then allowed to spill back into the natural water system of the area.

Western coal often contains sizable quantities of alkali and alkaline earth oxides which upon contact with water provide basic solutions. Talbot and coworkers (2) studied the pH change of several suspended ash slurries with time. They looked at systems both open and closed to the atmosphere. They noted that in the open system there was a dramatic initial increase in pH, with hopper ash exhibiting the most change. After one week their slurries equilibrated at a pH of approximately 8.5. With the closed system they reported the same pH increase but it took several weeks to decline. Green and Manahan (3) dissolved ash in mineral acid, allowing the ash to equilibrate overnight and then back-titrated with NaOH. They reported the fly ash dissolved in discrete steps of increasing acidity, indicating the presence of specific fractions in the material. The authors also stated that scatter of data typified in their plots was due to sample inhomogeneity and uncertain pH readings in the fly ash suspensions. Compensation was made by taking large numbers of data points.

Generally, the nature of coal ash is nonvolatile, inorganic matter.

Figure 2

Schematic of an Ash Pond.



In 1977 Dreesen and coworkers (1) analyzed and found some components of ash, including such toxic elements as boron, arsenic, fluorine, molybdenum, and selenium, to be leached with water. They proved this by sampling the effluent waters of the Los Alamos, New Mexico power plant and comparing the results with samples of the influent waters. They found elevation of these elements in the effluents. For example, intake river water contained less than $0.1 \mu\text{g}/\text{ml}$ of boron but ash pond effluents contained $12.0 \mu\text{g}/\text{ml}$ and cooling lake effluents contained $0.95 \mu\text{g}/\text{ml}$ boron.

Analyses of ash content have been extensively reported and compared using a variety of analyses techniques (4-7). Ash and its parent coal vary greatly in exact content from sample to sample, but the major components can be summarized from the reports of analyses in the literature. The major component analyses condenses to: silica, calcium, aluminum, magnesium, iron, potassium, and sodium. Many trace analyses are also reported in these papers.

Other interesting interpretations of ash content have been added to the literature through the use of electron micrographs. By radiating at selected wavelengths the major component concentrations can be photographed (4,5).

In a unique study, Furr and others (7) grew cabbages in soil amended with seven percent coal ash from twenty-one coal burning power plants. They measured uptake of the toxic elements by the

cabbages. The concentrations in the cabbages of arsenic, boron, molybdenum, selenium, and strontium showed high correlation with those in the ash.

This study involves one trace component of coal ash, boron. Interest in boron comes from the fact that, although it is an essential trace nutrient for plants (8), it becomes toxic at concentrations greater than one part per million (9,10).

Boron is a rare element in the earth's crust and is most abundantly associated with fossil fuels such as oil and coal with geothermal waters (11). Boron is always found in trace amounts in natural water systems. Most natural waters contain less than one half of a part per million with slightly higher concentrations found in geothermal waters and waterways through coal rich areas (12).

Few authors have looked specifically at the relationship of boron leaching in aqueous systems. Cox and others (13) looked at boron released from coal ash. They determined total boron by dc-arc emission spectrometry. Over a sixty second span they measured boron released at pH 4.55 and pH 7.40. They reported fifty percent of total boron, which could be as high as 1900 ppm, was leached into water. They also reported the quantity of boron leached was independent of pH over the range of 6 to 8 but availability was greater in acid. Also in this paper, they suggest that thermal fixation of the boron into an insoluble chemical state could be obtained by treating the ash at

1200°C for thirty minutes.

Choi and Chen (14) reported the amount of boron leached from four common adsorbents; hydro Darco, Eiltrasorb, activated bauxite, and activated alumina, as a function of pH. For all but one adsorbent the amount of boron leached at 25 g/l increased as pH decreased below pH 6 with boron leached remaining approximately constant above pH 6.

Part of the variability in analyses of ash can be improved by fractionation of particle size. There is a relationship between the size of the ash particles and their elemental composition. Electron micrographs done by Smith (15) and Campbell (4) showed ash to be an amorphous, fragile material composed of many particle sizes, shapes, and densities. Two separate reports (16,17) group the ash into three mass-size distributions. Those elements associated with large particles ($>20.0 \mu\text{m}$) are depleted relative to the original coal composition; a second group of elements in the intermediate size fraction ($20.0\text{-}6.0 \mu\text{m}$) have similar concentrations in ash and parent coal; and a third fraction of small particles ($6.0\text{-}2.5 \mu\text{m}$) contain elements including boron, which have enriched concentrations in ash.

Another group (18) which studied size fractionation defined seventeen size fractions in ash ranging from $10 \mu\text{m}$ through submicron in size. Their results showed that volatile trace elements increased in concentration with decreasing particle size above one micron; but,

for submicron particles the concentration becomes independent of particle size. These are significant findings since small particles are most easily suspended in water and the enriched boron content is easily released.

The adsorption characteristics of boron onto soils has been extensively studied. In a series of papers, Harder (19-21) studied boron in sediments and associated it with the clay mineral, illite. His primary concern in these studies was of agricultural significance so pH and temperature were not monitored. He did however, note that boron uptake was rapid at first and then gradual after a few hours.

In 1964 Hingston (22), also interested in the study of natural sediments, investigated boron adsorption onto illite, kaolinite, and montmorillonite. He studied boron uptake as a function of pH over the range of 3.8 to 10.5 and as a function of concentration. He was the first to suggest that boron adsorption exhibited Langmuir behavior. Couch and Grim (23) also studying the clays; illite, kaolinite, and montmorillonite, determined that the initial boron concentrations and temperature had a direct relationship on boron uptake.

Metwally (24) studied boron adsorption onto freshly precipitated aluminum hydroxide as a function of pH. Sims and Bingham (25) followed this procedure but also reported an inverse relationship between boron uptake and aging of the precipitate. A similar paper by McPhail and others (26) confirmed Sims' results.

Concurrent with these studies, several investigators while looking at volcanic soils in Chile, Hawaii, and Mexico (27-29) correlated a high boron adsorption by these soils with high concentrations of aluminum in them.

In addition to aluminum hydroxide, freshly precipitated iron hydroxide was studied for boron adsorption by Metwally (24) and by Sims (25,30,31). Iron is also capable of participating in the adsorption of boron but has 200 times less capacity for adsorption than does aluminum.

Bingham and Page (32) reported that sulfur and phosphorous exhibited no influence upon the adsorption of boron by an allophanic soil.

Choi and Chen (14) reported that calcium (II) ions and magnesium (II) ions showed an effect on boron adsorption with some adsorbents.

An increase in the concentration of calcium (II) ions to a certain value resulted in a decrease in the removal of boron for all adsorbents studied. The value was dependent upon the adsorbent used. Little or no additional effect was found with further increase in the concentration of calcium (II) above the value. For example, Filtrasorb removed boron less efficiently in the presence of calcium (II) ions up to a concentration of 100 mg/l but showed no further influence with increasing calcium (II) concentration. Magnesium (II) ions effected boron removal only when Filtrasorb was the adsorbent. Silica has been suggested in several papers (2,29,32) to exhibit a competitive effect with boron for the adsorption sites. Theis and Wirth (33) suggested

that some species of manganese may play a role in the adsorption of boron.

Choi and Chen (14) examined the effects of pH upon leaching of boron from the adsorbents and conversely the pH effects upon adsorption of boron onto the adsorbents. They reported increasing boron leached below pH 6 and approximately constant amounts of boron leached for all adsorbents between pH 6 and 9. They reported the optimum pH for adsorption of boron was dependent upon the adsorbent present and upon the concentration of boron in solution. In the same paper, they reported that salinity effected removal efficiency of boron. Removal efficiency decreased sharply and the pH at which removal is most efficient, increased sharply with increasing salinity up to 8% for hydro Darco, 5% for Filtrasorb, 8% for activated bauxite, and 10% for activated alumina. Above these concentrations no further decrease in removal efficiency and increase in pH was noted.

All of the previous adsorption studies used soil or some well-characterized surface as the adsorbent. In this study the ash was examined as a participant in the adsorption process. The mobility of boron in an aqueous system has been shown to be influenced by: pH, temperature, type and amount of adsorbing solids, the shape and density of the ash, and other chemical species present.

STATEMENT OF THE PROBLEM AND RESEARCH OBJECTIVES

Boron is one of the toxic elements in coal ash which is readily leachable into an aqueous system. The determination of the mechanism of boron mobility in a natural system involves many factors. A mechanism has been suggested to involve the adsorption and desorption of boron species from solid surfaces. Many conditions can influence such a process and need to be studied specifically. What type of soil or ash are present and does total concentration of these effect the efficiency of the system? What is the species of boron involved and what is its solubility in water? What are the maximum limits of the adsorption and desorption? And it must be determined if the process is simple reversible or if some parameters such as pH, time, and temperature effect the forward and reverse sequences differently.

Boron adsorption and desorption from soils has been studied by many workers. Few people have looked at the role of boron from coal ash. In this study, investigations were undertaken to determine the influence of pH, time, and ash type upon boron leachability. The influence of particle size upon a variety of components was studied. Ash concentration was varied and was determined to have a significant effect upon the amount of boron released. The boron retained was calculated and total availability of boron was then experimentally determined. Based upon the enhanced leachability of a variety of

major components with acid, analyses of total availability of these components was made. Iron and aluminum were specifically studied.

Further investigation of retained boron lead to adsorption experiments. Adsorption was studied by water conditioned ash and acid conditioned ash. The effects of pH upon the process were also determined. Additionally, releaching of the adsorption samples was investigated to determine changes in the ash after adsorption had taken place.

EXPERIMENTAL SECTION

Ash samples were obtained from the Boundry Dam Power Station near Estevan, Saskatchewan, Canada, and from a test burn of coal to be used at the Poplar River Power Project in southern Saskatchewan. A description of the ash samples is presented in Table 1. The ash samples were passed through 100 mesh screen prior to leaching. Particles were manually fractionated with the use of concentric sieves. The sieve sizes were 100, 140, 200, and 325 mesh. The mesh sizes correspond to openings of 150 μm , 125 μm , 75 μm and 45 μm , respectively. All adsorption studies were done on ash which passed through the 325 mesh sieve.

Whenever possible all procedures were carried out in polypropylene or teflon containers to avoid any possibility of leaching boron from glassware, especially at extreme pH values or elevated temperatures.

The leaching studies involved mixing 50.0 ml of leachate water, distilled or natural, with the desired amount of ash. The solutions were kept in polypropylene beakers covered by watch glasses. This provided for exchange of carbon dioxide. Water lost by evaporation was replaced through the regular addition of doubly-distilled water. At the desired time interval, an aliquot of leachate solution was withdrawn and analyzed. A Parr, teflon-lined bomb was utilized to digest the ash samples when elevated temperatures and HF were used.

Table 1

Description of Ash Samples.

<u>Sample</u>	<u>Description</u>
A1	Bottom Ash--Poplar River
A2	Upper Ash--Poplar River
A3	Dust Ash--Poplar River
A4	Upper Ash, 5-day composite, Boundry Dam
A5	Bottom Ash, 5-day composite, Boundry Dam
A6	Composite: A1 (23.5%), A2 (4.7%), A3 (71.8%), Poplar River
A7	Composite: A4 (58%), A5 (42%), Boundry Dam

Adsorption experiments involved suspending the ash samples in solutions of known boron concentration and measuring the decrease in solution boron concentration after forty eight hours.

Ash was conditioned for the adsorption experiments by leaching 25 grams with three liters of doubly-distilled water. This was done in three consecutive liter portions for one and one half hours each. The ash was filtered and air dried. The acid conditioned ash prepared by the same procedure was mixed with one molar HCl or HNO₃ and immediately filtered and dried. Adsorption experiments were carried out in covered polypropylene bottles to minimize evaporation. Sodium borate was used as the standard boron reference. Adsorption experiments were allowed to equilibrate for two days before measurement. The adsorption experiments were done at fifty five grams of ash per liter and in 10 ml portions. The releachings of the adsorbent were in 5 ml portions.

Ash was succesively washed for a determination of total release of components to leachates. One gram of ash was subjected to washes in one liter of 1 M HNO₃, 1 M NaOH and doubly-distilled water. Samples were then shaken on a mechanical shaker for twenty four hours, centrifuged for twenty minutes at nine thousand rpms, and decanted. This procedure was repeated for a total of three washings. The nine leachates were analyzed separately.

Solution pH was adjusted with additions of variable concentrations

of NaOH or HNO_3 for the leaching experiments. For the adsorption experiments buffers were used. The buffers used were: Trizma base [Tris (hydroxymethyl) amino methane], phosphate buffer, ammonia buffer, and acetate buffer.

All reagent solutions were prepared using doubly-distilled water. Unless otherwise specified, all experimental solutions were also made with doubly-distilled water.

All natural water samples were filtered through 0.45 micron filters prior to use. The natural water obtained from the Boundry Dam Project had the following characteristics: pH = 8.25, specific conductance = 740 $\mu\text{mhos/cm}$, $\text{HCO}_3^- = 2.4 \text{ mg/l}$, $\text{SO}_4^{2-} = 210 \text{ mg/l}$, $\text{Cl}^- = 10.3 \text{ mg/l}$, $\text{Ca} = 4.4 \text{ mg/l}$, $\text{Mg} = 22.3 \text{ mg/l}$, $\text{K} = 11.2 \text{ mg/l}$, $\text{Na} = 92.2 \text{ mg/l}$, $\text{B} = 0.343 \text{ mg/l}$. The natural water obtained from the Poplar River had the following characteristics: pH = 8.30, specific conductance = 986 $\mu\text{mhos/cm}$, $\text{HCO}_3^- = 406 \text{ mg/l}$, $\text{SO}_4^{2-} = 189 \text{ mg/l}$, $\text{Cl}^- = 6.0 \text{ mg/l}$, $\text{Ca} = 33.0 \text{ mg/l}$, $\text{Mg} = 33.9 \text{ mg/l}$, $\text{K} = 9.8 \text{ mg/l}$, $\text{Na} = 140 \text{ mg/l}$, $\text{B} = 0.820 \text{ mg/l}$.

Boron concentrations were evaluated by the curcumin method utilizing drying at 75.0°C. The sensitivity of the adsorption experiments lead to an examination of nitrate interference. Nitrate was determined to yield erroneously high results which are significant when working in the lower limits of sensitivity of the curcumin method of boron analyses. Hydrochloric acid was utilized for all acid related portions of the adsorption experiments. Atomic adsorption spectrophotometry, with

appropriate radiation buffers, was used to determine sodium, potassium, calcium, magnesium, aluminum, cadmium, chromium, copper, manganese, lead, and iron. Bicarbonate was determined by HCl titration, and pH was monitored by a Radiometer M-26 pH meter using glass-SCE electrodes. Sulfate was determined by colorimetric titration (38) and chloride by iron-thiocyanate procedure. Table 2 contains a summary of these procedures. The standard curve for the boron analyses, curcumin method is presented in Figure 3.

Table 2

Analytical Procedures.

Specific Conductance	Determined by standardized probe and corrected to 25°C.
pH	Measured by standardized electrodes, glass and SCE reference.
HCO ₃ , CO ₃ , OH	These are determined potentiometrically (pH) by titration with standard acid.
SO ₄	Titration with standard barium using nitrosulfazo III indicator for equivalence point detection.
Cl	Spectrophotometric using Hg(SCN) ₂ and Iron (III).
NO ₃	Brucinic sulfate and/or spectrophotometric method.
Na, K, Ca, Mg	Determined by atomic absorption spectrophotometry using appropriate radiation buffers.
SiO ₂	Spectrophotometric using molybdo-silicate procedure.
Boron	Curcumin method, spectrophotometric with color development at 75°C.
Al, Cd, Cr, Cu, Fe, Mn, Pb, Zn	Determined by atomic absorption spectrophotometry.

