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The Chemical Composition of Black Powder Substitute

presented by

Jennifer Marie Yezek

has been accepted towards fulfillment
of the requirements for

Master of Science degree in Criminal Justice

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THE CHEMICAL COMPOSITION OF BLACK POWDER SUBSTITUTES

By

Jennifer Marie Yezek

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

Department of Criminal Justice

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ABSTRACT

THE CHEMICAL COMPOSITION OF BLACK POWDER SUBSTITUTES

By

Jennifer Marie Yezek

The challenge at a bombing or other explosion scene is to determine the type of destructive device and filler used. A strong percentage of improvised explosive devices used in bombings in the United States incorporate the use of the low explosive, black powder. Unfortunately, there are many problems with using black powder due to its lower ignition temperature, its poor efficiency, and its time-consuming and dangerous production. Thus, black powder substitutes are also being used as fillers. In order to determine the existence of black powder substitutes in evidence, their chemical properties must be known. This chemical characterization can be successfully completed using several techniques on both the intact powder and the residue. The useful characterization steps are x-ray diffraction (XRD), spot tests, ion chromatography (IC), capillary ion analysis (CIA), and high performance liquid chromatography (HPLC). These tests will be run on Golden Powder, Black Canyon Powder, Black Mag Powder, and Clean Shot Powder. Black Powder and Pyrodex^{R} will also be tested for confirmation and comparison purposes. After determining the compositions of the black powder substitutes, analysts will be able to use the information to eliminate certain sources and identify possible sources in low explosive cases.

TABLE OF CONTENTS

Percentage

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Analytical C

Description

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Intact Comp

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LIST OF TABLES

Schematic c

Schematic c

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LIST OF FIGURES

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The Chemical Characterization of Black Powder Substitutes

Introduction

The primary challenge at a bombing or other explosion scene is to determine whether the act was accidental or intentional. If the latter, the examiner must then try to determine the type of destructive device and filler used. A significant percentage of improvised explosive devices used in bombings in the United States incorporate fillers of low explosives such as black powder.[1] According to prior and recent statistics outlined in the Bureau of Alcohol, Tobacco, and Fiream's *Arson and Explosives Incidents Report*, the most recent yearly percentages for usage of black powder as a filler in destructive devices are as follows:

Table 1. Percentage of Black Powder Used as Filler[2]
(Percentages adjusted to include only destructive devices and to avoid duplicate recordings)

YEAR	% Black Powder
1993	27
1994	35
1995	23
1996	20
1997	19

Due to the knowledge of the products and reactants of black powder, trained laboratory personnel and investigators can and do determine the nature of the explosive(s) used in the device(s) at bombing scenes. However, there is not an abundance of information available on black powder substitutes. The scant information found was obtained from gun magazines, which are concerned mostly with the ability of black pow

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black powder substitutes to perform in hunting and competitive shooting situations. There was even less information found about the chemical composition and properties of the substitutes in the few relevant academic papers.

Despite the shortage of available information, there is a definite need for the forensic community to understand the chemical composition of black powder substitutes. As users of black powder become more irritated with its shortcomings, they will begin to turn to black powder substitutes. These substitutes will then become more readily available on the market. Since the majority of cases received at ATF labs are pipe bombs, many of which contain black powder or Pyrodex[R], there is a distinct possibility that these same black powder substitutes used in muzzle-loading firearms will appear in future pipe bombs as well.

To determine the existence of fillers in arson and explosive cases, their chemical properties must be known. There is virtually no literature on either the chemical composition of the pure black powder substitutes or their residues. None of the literature individually or collectively serves to provide a justifiable chemical characterization of the substitutes. Thus, it is extremely beneficial to perform various chemical tests on both the intact powders and their combustion residues in order to characterize the powders.

Background Information

Black Powder

Originally used in simple blasting operations, black powder is a ternary mixture of 75 KNO_3: 15 charcoal/carbon black: 10 sulfur. This approximate 6:1:1 composition has not changed drastically since 1781.[3] Deviating considerably from this formula produces burning that is much slower and much less vigorous. Potassium nitrate serves as the oxi

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as the oxidizer, while charcoal and sulfur serve as the combustible materials, or fuels. The color of black powder is initially dark gray. When tumbled with graphite, or carbon black, to glaze the surface, it becomes black. Black powder is non-porous and burns from the surface, which becomes progressively smaller as the burning continues. The white smoke contains small, solid particles. Although the percent composition of the burned powder by volume varies from source to source, general guidelines are as follows:

Table 2. Burned black powder composition[3]

Gaseous Products	%	Solid Products	%
Carbon dioxide	49.29	Potassium carbonate	61.03
Carbon monoxide	12.47	Potassium sulfate	15.10
Nitrogen	32.90	Potassium sulfide	14.45
Hydrogen sulfide	2.65	Potassium thiocyanate	0.22
Methane	0.43	Potassium nitrate	0.27
Hydrogen	2.19	Ammonium carbonate	0.08
		Carbon	8.74
		Sulfur	0.08

The chemical reactions that occur during combustion are complex. These reactions have been extensively studied with sometimes unequivocal results.[4-8] Since the major products result from the oxidation of sulfur and charcoal, the extent of this oxidation influences the variety and intensity of intermediate products observed. The extent of the oxidation is itself influenced by the combustion or explosion conditions.

Tenny L. Davis, in his chapter on black powder in the book, Chemistry of Powder and Explosives, states the uses of black powder as the following:

> It is used in petards, as a base charge or expelling charge for shrapnel shells, in saluting and blank fire charges, as the bursting charge of practice shells and bombs, as a propelling charge in certain pyrotechnic pieces, and, either with or without the admixture of other substances which modify the rate of burning, in the time-train rings and in other parts of fuses.[3]

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In this country, the use of black powder as a blasting powder has been supplanted by blasting powders containing sodium nitrate. With this shift in function, the ballistic effects of black powder have become even more important. Black powder functions as the propellant in muzzle-loading firearms. Due to dangerous pressures, smokeless powders cannot be substituted for the propellant.

Recently, black powder firearms have become more popular. They require a closer range for hunters. This closer range expands hunting opportunities for ethically hunting most game in North America. Due to this renewed popularity of black powder, retailers are offering more muzzle-loading products and states are offering special hunting seasons. There are also several magazines devoted to black powder, such as *Black Powder Cartridge News* and *Black Powder Journal.* Other magazines, such as *Field and Stream* and *Handloader,* regularly cover black powder shooting and hunting.

Unfortunately, there have been many claims about problems encountered with black powder. With its lower ignition temperature of 300°C, it is extremely sensitive to impact friction. Thus, handling and storage procedures must be strictly observed. There have also been concerns over the ability of black powder to build up residue between shots, or fouling. Other claims cite the presence of observable corrosive material. Additionally, black powder combustion products are 56 percent solid materials.[9] This high amount of solid combustion products results in poor efficiency and huge amounts of unpleasant smoke. Finally, the manufacture of black powder requires heavy and expensive material as well as being time-consuming and dangerous.

Throughout recent history, improvements have been sought for a cleaner, flashless, smokeless, and noiseless powder. Although smokeless powder is safer to handle a

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handle and store, it can produce dangerously high pressure levels if too much propellant is used. Thus, the invention of a product with the low pressure characteristics of black powder and the safer characteristics of smokeless powder would be greatly appreciated in the firearms community.

Since the 1970s, there have been many patents dealing with new methods and compositions of explosives.[9-11] These altered compositions suggest an emergence in the presence of black powder substitutes. For example, Patent US04497676 states:

> A gunpowder substitute which is capable of also being molded into a consumable cartridge or cartridge case comprising between 50% to 75% by weight of an inorganic nitrate and between 25% t0 50% by weight of an organic acid including ascorbic acid, erythorbic acid and mixtures thereof.[10]

Or similarly:

> A pyrotechnic composition useful for gunpowder, propellant or explosive purposes, which comprises an organic acid such as ascorbic or erythorbic acid, a nitrate salt oxidizer, and about 6-15% of potassium perchlorate, has improved properties including reduced residue.[11]

The basic principle in developing a black powder substitute is mixing an oxidizing salt with a combustible material. One black powder substitute, Pyrodex^R, is a commercial success patented by the Hodgdon Powder Company. It claims to burn cleaner and alleviate the fouling and clean-up procedures between shots necessary with black powder. It also claims to provide more consistent pressure and velocity as well as being less sensitive to ignition.[12] With its success and the recurring inconveniences of black powder, it is highly probable that other black powder substitutes will appear on the explosives market as long as funds are available for the necessary research and development. Currently, both information and availability of black powder substitutes are extremely scarce. An exhaustive search for more information on these substitutes was only slightly productive. Besides the commercially successful Pyrodex^R, there is no mention of the chemical composition of the other black powder substitutes in any of the examine

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examined literary materials. Thus, the only available information relies on the observations and claims of effectiveness listed in the following section.

Attempts to contact the manufacturers were fruitless. For Black Canyon, Golden Powder, and Black Mag there was no response to phone calls, letters, or e-mail inquiries. The response to an e-mail for more information on Clean Shot read as follows:

> Unfortunately, we can not release the ingredients in our product and the percentages for a study to be published as a thesis. We only release this information after we have obtained a confidentiality agreement from the person, organization, or government agency to which we release the information. Our patent application for this product has not been granted yet and for that reason we do no disclose this information without the confidentiality agreement. Our confidentiality agreement specifically states that any information that is released can not be published or used in any way that would cause harm to our organization. We hope that you understand that this precaution is taken because of the significant amount of money that went into developing our formulation and how releasing this information could harm our company.

An e-mail from Clear Shot related the same information. Although there was no successful avenue for obtaining information from any manufacturer, the addresses and phone numbers used for contact purposes are listed below.

Black Powder Substitutes

1. Black Canyon Powder[13,14]

Manufacturer: Legend Products Corporation; Las Vegas, NV 89125; 702-593-6722

Claims: heavy compression necessary in order to work properly; sweet, non-toxic taste; equivalent weight to black powder

Observations: no staining, leading, or fouling after 25 shots; consistent, slightly higher velocities; moisture resistant; more complete burn due to higher burning rate

Concerns: problems with clean-up and storage; green and blue oxidation formed when brass is left uncleaned; film of orange dust formed at the breech end of the rifling; must be loaded by weight, not volume; only comes in one granulation; extremely hydrophylic; only one granulation available

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2. Black Mag Powder[15]

Manufacturer: Arco Company; P.O. Box 101, Mayor, FL 32066; 904-294-3882

Claims: moisture resistance; faster ignition; consistent velocity; non-corrosive; non-fouling; safe; non-toxic; and clean

Observations**:** lower peak pressure; no noticeable residue after swabbing with two patches; quick and dependable ignition; no signs of rust formation; slower burn

Concerns**:** $25.00 per pound; very difficult to find

3. Clean Shot Powder[16,17]

Manufacturer: Clean Shot Technologies, Inc.; 21218 St. Andrew's Boulevard, Suite 504, Boca Raton, FL 33433; 888-886-2532; www.cleanshots.com/product.htm

Claims**:** no nitrocellulose; no sulfur fouling, corrosion, or odor; no cleaning necessary between shots; safer than black powder; similar ballistic pressure curves to black powder

Observations**:** no fouling build-up; less cleaning time; accurate; no swelling of cases

Concerns**:** indeterminable "shelf-life"; overloading creates dangerous pressures; sensitive to moisture and humidity; threatening ignition and combustion problems

4. Clear Shot Powder[18]

Manufacturer: Goex; P.O. Box 659; Doyline, LA 71023-0659; 318-382-9300

Claims**:** contains no ascorbic acids or perchlorates; clean burning; non-corrosive; not hygroscopic; indefinite shelf life; consistent velocities; low pressures; easy clean-up

Observations: **none**

Concerns**:** impossible to find despite claims of its availability in 1999

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5. Golden Powder[12,19]

Manufacturer: Golden Powder International; 701-1470 Pennyfarthing Drive, Vancouver, B.C., Canada V6J4Y2; 604-731-4637

Claims: even burn rate; able to be compressed, formed, and handled lead to various applications; non-corrosive

Observations: lab reports show it will perform; black stuff in bore was wiped out

Concerns: difficult to obtain; no performance figures

6. Pyrodex[12,20]

Manufacturer: Hodgdon Powder Company; P.O. Box 2932, Shawnee Mission, KS 66201; 913-362-9455

Chemical Composition: potassium nitrate, potassium perchlorate, sodium benzoate, and dicyandiamine

Claims: more shots per pound; cleaner burn which alleviates fouling and the need to clean between shots; consistent pressures and velocities; performance comparable to black powder; safer alternative to black powder; less sensitive to ignition

Observations: much less fouling than black powder

Concerns: still some fouling; no significant improved performance over black powder

Experimental

Samples of Goex Black Powder FFFg, Pyrodex RS, Clean Shot Powder, and Black Mag Powder were obtained from the low explosive collection at the Bureau of Alcohol, Tobacco, and Firearm's National Laboratory Center in Rockville, Maryland. Samples of Golden Powder and Black Canyon Powder were obtained from reference samples in a collection compiled by Charles Midkiff, a senior forensic chemist at the ATF National Laboratory Center.

Samples of all six powders were burned in open air and atmospheric pressure conditions. In order to obtain burned residue from the powders, .05g of each substitute powder was placed in the bottom of a clean crucible. Once the crucible was placed in a hood, a wooden stick was lit and quickly placed in the powder. The residue was recovered from the crucible by using approximately 10-20 mL deionized (DI) water. This mixture was then filtered for purity and the filtrate was diluted to suitable concentrations for analysis.

Five different analyses were performed on the six powders and are outlined below. Each analysis was performed on both the intact powder and the burned residue with the exception of x-ray diffraction and capillary ion analysis. These two tests were only run on the intact powder. In the case of x-ray diffraction, there was an insufficient amount of residue from the powder combustion for analysis. In the case of capillary ion analysis, there was a limited amount of personnel knowledgeable in the operation of the instrument and its intracacies.

Additionally, several physical properties of the intact powder particles were observed visually. Since this observation was done only with the naked eye and a low-power (12X), binocular laboratory microscope, its findings will be recorded in the results section without further discussion.

X-ray Diffraction (XRD)

The original samples of the intact powder were crushed using a mortar and pestle. The sample was then placed evenly in the well of a slide. The analyses were performed using a Scintillation Phillips 3100 X-ray Generator (XRG) and a Long Fine Focus Cu Anode X-ray tube. 45 volts and 35 amps were applied to each powdered sample. Each sample was then measured from an angle of 5 degrees to an angle of 60 degrees.[21] The approximate run time was 30 minutes.

Spot Tests

Ammonium Ion, Nitrate, Nitrite, Oxidizer, Perchlorate, and Thiocyanate Tests

2-3 drops of the reagent were added to 4-5 drops of the sample powder in a white spot plate using a disposable pasteur pipette. Charles Midkiff prepared the reagents listed below:

Ammonium Ion Test[22]

1. *Nessler's Reagent*- A.P.H.A. (Fisher SO-N-16 or equivalent)

Nitrate and Nitrite Tests[22]

1. *Sulfanilic Acid Solution*- 1g ACS Reagant Grade Sulfinilic Acid by warming in 100 mL of 30% acetic acid (aqueous)
2. *N-1-naphthylethylemediamine dihydrochloride Solution*- 1g of ACS Reagent Grade in 100 mL of 70/30 ethanol/acetic acid solution.
3. *Zinc Powder*- fine

Oxidizer Test[22]

1. *Sulfuric Acid*-18M- ACS Reagent Grade
2. *Diphenylamine*- 1g in 100 mL concentrated sulfuric acid

Perchlorate Test[23]

1. *Methylene Blue*- 0.03-0.05% aqueous solution

Thiocyanate Test[24]

1. *Ferric Chloride Solution*- 1g ACS Reagent Grade $FeCl_3$ in 10 mL high resistance deionized water, 10% aqueous

Chlorate and Sulfide Tests

After acidifying 3-4 drops of the sample powder with 1-2 drops of 6N nitric acid, 2-3 drops of the reagent were added to the acidic sample in a small glass vial using a disposable pasteur pipette. Charles Midkiff prepared the reagents listed below.

1. *Silver Nitrate Solution*- 1g ACS Reagent Grade $AgNO_3$ in 100 mL of high resistance deionized water, 1% aqueous
2. *Nitric Acid*- 20 mL ACS Reagent grade HNO_3 to 50 mL high resistance deionized water, 6N

Sulfate Test[23]

After acidifying 3-4 drops of sample powder with 1-2 drops of hydrochloric acid, 2-3 drops of the reagent were added to the acidic sample in a small glass vial using a disposable pasteur pipette. Charles Midkiff prepared the reagents listed below.

1. *Barium Chloride Solution*- 5g ACS Reagent Grade $BaCl_2$ in 100 mL high resistance deionized water, 5% aqueous

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2. *Hydrochloric Acid*- 25 mL ACS Reagent Grade HCl in 50 mL high resistance deionized water, 6N

Sulfur Test[24]

After weighing several grains of the sample and a piece of filter paper, the sample is rinsed with approximately 10-20 mL of hot water. After allowing the filter paper to dry and re-weighing it, the sample is then rinsed with approximately 10-20 mL of pyridine. Finally, the filter paper is dried and re-weighed one final time. The loss in weight is recorded.

Ion Chromatography (IC)

The original samples of the intact powder and burned residues were diluted with DI water until they produced a reading of approximately 50 ppm on a Fisher Scientific Digital Conductivity Meter. The samples were then placed in individual 0.5 mL vials and arranged into a cassette. This cassette was mounted in a Dionex AS40 Automated Sampler connected to the IC. The analysis was performed on a Dionex CX 500 Ion Chromatograph equipped with a 25 μl injection loop, a DS-3 Conductivity Cell Detector, and a ASRS-ULTRA Auto Self-Regenerating Suppressor.

The analytical separation of chlorate, nitrite, chlorate, nitrate, phosphate, and sulfate were performed with Dionex columns: Dionex 4 mm AS11 Ion Pac Analytical Column, Dionex 4 x 50mm AG11 Ion Pac Guard column, and an Anion Trap Cartridge (ATC). The eluent was sodium carbonate. The analysis time was 22 minutes.

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For the analytical separation of thiocyanate and perchlorate, the following Dionex columns were used: Dionex 4 x 250mm AS16 Ion Pac Analytical Column, Dionex 4 x 50mm AG16 Ion Pac Guard column, and an Anion Trap Cartridge (ATC). The eluent is 60mM KOH which flowed at a rate of 1.0 ml/min. The analysis time was 15 minutes and run at a temperature of 30 degrees Celsius.

Cation separation was also performed using the following Dionex columns: Dionex 4mm CS12 and Dionex 4 x 50mm CG12 Guard Column. The isocratic system used 15mM Methanesulfonilic Acid (MSA) as its mobile phase. Please refer to Figure 2 for a schematic diagram of the IC instrumentation used in the tests.

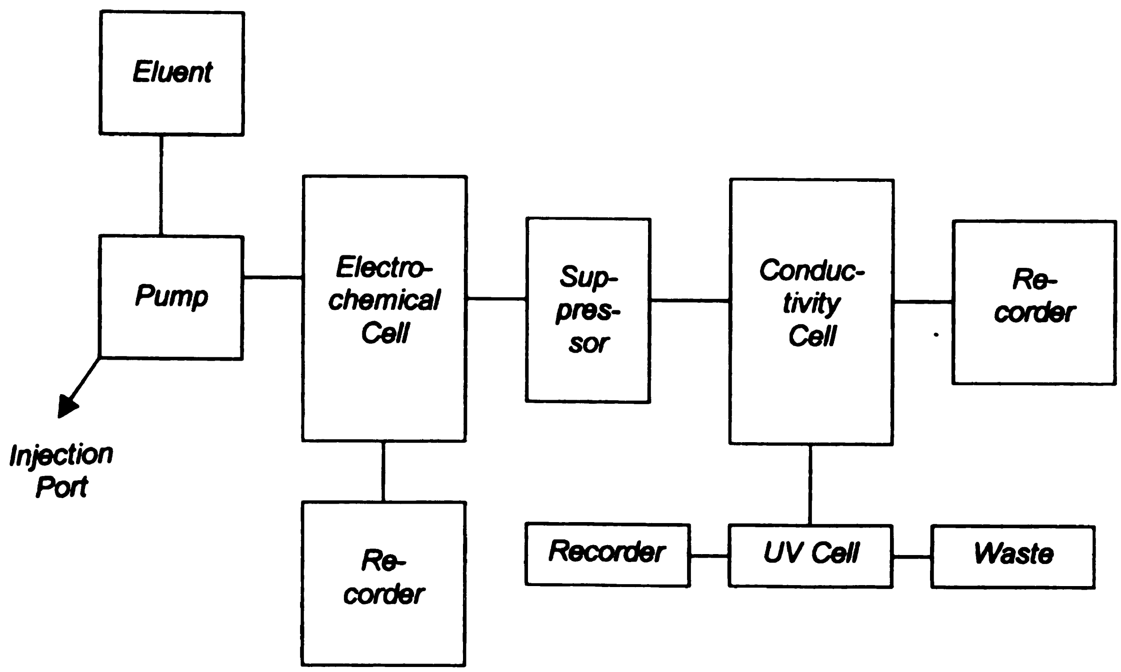

Figure 2. Schematic of Ion Chromatograph for cation analysis.[25]

For cation analysis, the suppressor column contains a strongly basic exchange resin in the hydroxide form. This basic exchange resin is necessary for two important conversions. First, the conductive species hydrochloric acid is converted into water as seen in reaction 1 below. Second, the cations present in the sample (Y^+) are converted into their corresp

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corresponding bases, which are free to migrate through the column. The illustrative reactions are listed below.[26]

1. $Resin\text{-}N^+OH^- + H^+Cl^- \longrightarrow Resin\text{-}N^+Cl^- + H_2O$

2. $Resin\text{-}N^+OH^- + Y^+Cl^- \longrightarrow Resin\text{-}N^+Cl^- + Y^+OH^-$

For anion analysis, the suppressor column contains a strongly acidic exchange resin in the hydrogen form. This acidic exchange resin is again necessary for two important conversions. Reaction 1 diagrams the conversion of the conductive species sodium bicarbonate into carbonic acid, which dissociates into water and carbon dioxide. Reaction 2 diagrams the conversion of the anions present in the sample (X^-) into their acidic forms.[26]

1. $Resin\text{-}SO_3^-H^+ + Na^+HCO_3 \longrightarrow Resin\text{-}SO_3^-Na^+ + H_2CO_3$

2. $Resin\text{-}SO_3^-H^+ + Na^+X^- \longrightarrow Resin\text{-}SO_3^-Na^+ + H^+X^-$

Capillary Ion Analysis (CIA)

The original samples of the intact powder were diluted with DI water until they produced a reading of approximately 15 ppm on the Fisher Scientific Digital Conductivity Meter. After 1 drop of the internal standard is added to the bottom of a sample vial, 0.5 mL of the sample is placed in the vial. The sample vials were then placed in a carousel in the autosampler. The analysis was performed on a Waters™ Capillary Ion Analyzer. Analytical parameters appear in Table 3 on the following page. A schematic diagram of CIA also appears as Figure 3 on the following page.

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Table 3. Analytical Capillary Ion Analyzer Parameters

Electrolyte	4.3 mM sodium chromate, 0.48 mM TTAB, pH8	Waters IonSelect™ Low mobility Cation Electrolyte (2-Hydroxyisobutyric acid, 4-methylbenzylamine, and 18-crown-6 ether)
Capillary	60 cm x 75 μm fused silica	60 cm x 75 μm fused silica
Power Supply	Positive Voltage	Negative Voltage
Applied Voltage	20 KV	15 KV
Internal Standard	Cesium	Barium
Detection	Indirect UV at 214 nm	Indirect UV at 254 nm

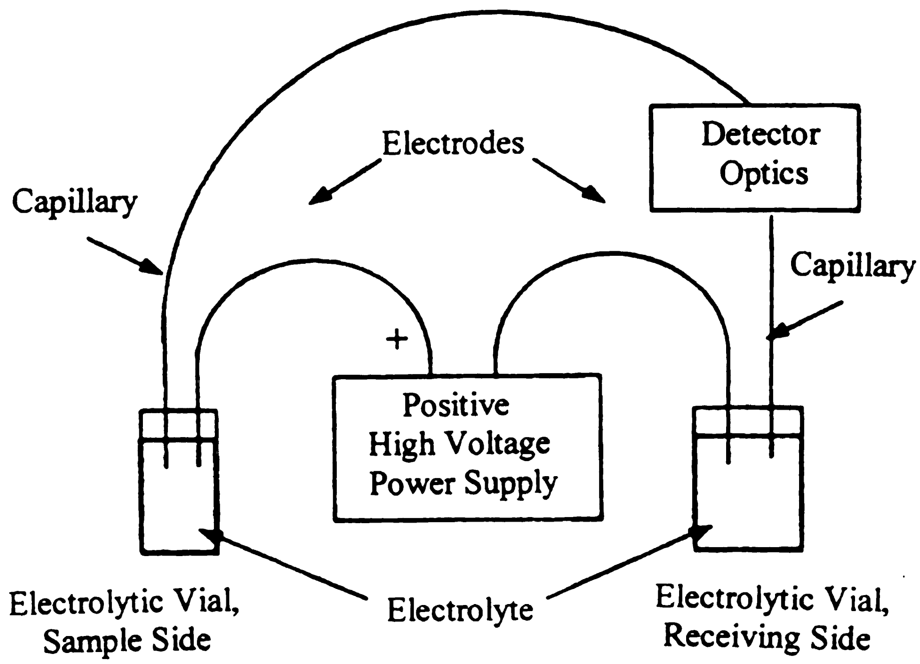

Figure 3. Schematic of Capillary Ion Analyzer[27].

High Performance Liquid Chromatography (HPLC)

The HPLC used to detect benzoic acid and/or dicyandiamide (DCDA) consisted of a Waters 6000A pump (Waters Associates, Milford, MA) and a Waters model 441 absorbance (UV) detector. The column used was a Polypore H*, 4.6mm x 100 mm.

manufactured by the Pierce Chemical Company (Rockville, IL). All solvents were HPLC grade. The chromatograms were recorded on a Hewlett-Packard HP3396 Series II Integrator.

The mobile phase was 10% methanol in .01N sulfuric acid. The eluent was pumped through the column at 1.0 mL/min and was monitored by the UV detector at 230 nm. Each sample was approximately 50 ppm with an injection volume of 5 μl. This procedure was used on the powder extracts and residues. Please see Figure 4 below.

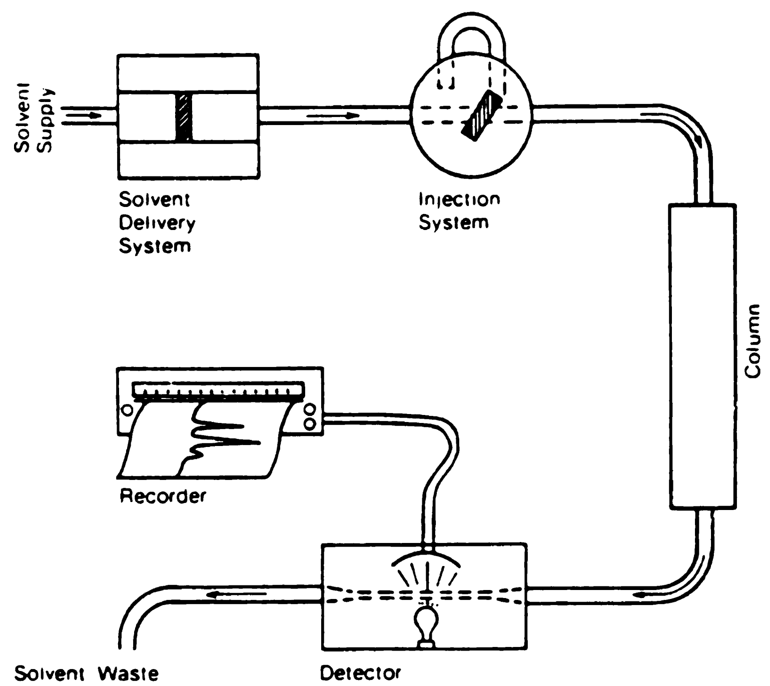

Figure 4. Schematic of High Performance Liquid Chromatogram[28]

Results

Visual Analysis

The results of this section were done quickly. The color was solely determined by the human eye, whereas the shape and texture of the particles were determined with the aid of a microscope. General results appear in the table on the following page.

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Please refer to the last page of Appendix I for photographs of all the powders except Black Mag. There was not a sufficient amount of this substitute powder for a suitable photograph.

Table 4. Description of Black Powders and its substitutes

	Color	**Shape/Texture**
Black Powder	Black	Pyramidal slabs
Pyrodex	Dark Gray	Stony, rounder
Golden Powder	Golden	Irregular, jagged
Black Canyon	Light brown	Stony, smoother
Black Mag	Tan	Stony
Clean Shot	Gray	Stony, blotched

X-ray Diffraction Analysis

If a crystalline material is present, x-ray diffraction can serve to characterize the compounds present. Due to the repetitive arrangement of atoms in a crystal lattice, the x-rays directed at these regions will diffract at a given wavelength to form a characteristic pattern. This analysis revealed several of the powders to be similar in composition. Potassium nitrate was present in all six powders. Both Golden Powder and Black Canyon powder also contained ascorbic acid. Clean Shot Powder and Black Mag Powder contained ascorbic acid and potassium perchlorate as well. The formula of Pyrodex^{R} is patented and contains sulfur, sodium benzoate, potassium nitrate, and potassium perchlorate. Black powder's composition has been known for several centuries to be potassium nitrate, sulfur, and charcoal. Please see Appendix II for relevant data.

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Spot Tests

These tests are an initial screening technique for suspected intact explosives and their residue. When a known reagent reacts with an unknown solution, a characteristic color or precipitate is formed. This result is then used for further identification of the anions and/or cations present. These tests are simple, requiring only disposable spot plates and pipettes, glass well slides, test reagent solutions, known anion and cation test solutions, and drops of the unknown solution. Please see Appendix III for complete results and observations.

When the ammonium ion is present in a strongly basic solution, NH_3 is liberated. When the Nessler's reagent, a mixture of KI and HgI_2, is mixed with ammonia, an orange red precipitate, $HgI_2 \cdot HgNH_2I$, is formed.[22] This color is indicative of ammonia salt. The only positive result for this test was the black canyon residue.

In an acidic solution, the chloride ion, a Group 1 anion, reacts with silver nitrate. Low concentrations produce turbidity while higher concentrations produce a white precipitate. The significant, positive results for this test were the residues of Pyrodex[R], Clean Shot, and Black Mag.

In a mildly acidic solution, nitrites react with primary amines to form diazonium cations, which result in highly colored azo dyes in further reactions.[22] The dyes produce an intense red color that is readily observable at low concentrations. This analysis is known as the Greiss Spot Test. The residues for all six of the powders tested were significantly positive.

Unlike nitrites, nitrates do not react with primary amines to form diazonium cations or colored azo dyes. However, when a reducing agent is added, nitrates can be reduced to nitrites and will then react to form the azo dyes.[22] Significant positive results for this spot test, coined the Modified Griess test, included all six of the powder extracts and powder residues. The extracts formed more intense colors than the residues.

Oxidizers can be detected by color formation when in the presence of diphenylamine in concentrated sulfuric acid.[22] This test is a preliminary screening analysis for the presence of nitrate, nitrite, and chlorate. Nitrate forms an immediate and permanent ultramarine. Both nitrite and chlorate form a dark blue color. However, this blue color fades to a yellow green in the presence of nitrites. Positive results indicative of nitrites were found in the residues for Pyrodex[R], Clean Shot, and Black Mag powders.

In the presence of the methylene blue cations, perchlorates form violet precipitates[23] This positive reaction was seen strongly in the water extracts of Pyrodex[R], Clean Shot, and Black Mag and less strongly in their residues.

When sulfates are placed in an acidic solution with barium chloride, turbidity ensues at lower concentrations and a white precipitate forms at higher concentrations.[23] Significant, positive results were obtained in the residues of black powder and Pyrodex[R]. Trace amounts were observable in the residues of Black Canyon, Golden Powder, and Black Mag. However, these results may be attributed to the use of a black powder-containing fuse for initiation.

The detection of thiocyanate is obtained by reacting it with ferric chloride in an acidic solution.[24] In this acidic solution, a blood red color is indicative of thiocyanate. Positive results were seen with black powder, Pyrodex[R], and Clean Shot residues.

The presence of sulfur in a black powder formulation can be determined. Once the potassium nitrate is dissolved in hot water and filtered out of the solution, pyridine is then ac

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then added. After the filter paper is dried, it is re-weighed. The difference in weight is equal to the amount of sulfur present. For Golden Powder, Clean Shot, and Black Canyon, the weight differences were all .01g. Thus, there was no sulfur present. The black material left on the filter paper was indicative of charcoal. However, it could not be scraped from the filter paper and thus not ignited for further confirmation.

Ion Chromatography

The ion chromatography system used in the ATF National Laboratory Center is capable of running anion and cation analysis simultaneously. The anion run for chlorate, nitrite, chlorate, nitrate, phosphate and sulfate is completed in 22 minutes while the anion analysis for thiocyanate and perchlorate is 15 minutes. Cation analysis for sodium, ammonium, potassium, magnesium, calcium, strontium, and barium is complete in 16 minutes.

With the installation of the autosampler, the time in between runs becomes reproducible and appears to improve reproducibility of the final, analytical results. The detectable anions and cations included in the standard are those ions characteristic of low explosives and their residues. Two separate anion analyses are used to prevent the use of a gradient system that can present many operational problems. Please see Appendix IV for relevant chromatograms.

Analysis of Anions by IC

As evident in Table 1, nitrate was present in the extracts of all six of the powders examined. Perchlorate was also evident in the extracts of Pyrodex^{R}, Black Mag, and Clean Shot.

In the residues of all six of the powders, nitrate was present. Additionally, black powder and Pyrodex^R residues indicated the presence of the thiocyanate and sulfate ions. Finally, Pyrodex^R, Black Mag, and Clean Shot residues also showed the presence of chloride and small traces of perchlorate.

Analysis of Cations by IC

The major cations detected in the extracts of the six powders were sodium and potassium. To a lesser extent, calcium was detected in each sample.

The ammonium ion was also present in the residues of Pyrodex, Golden Powder, Black Canyon, and Clear Shot. Traces of magnesium were also found in Clear Shot and Black Canyon.

Capillary Ion Analysis

This system achieves separation by applying a high-voltage potential across a 60cm x 75μm uncoated fused silica capillary with each end inserted in an electrolyte reservoir. The ions present in the sample migrate according to their electrolytic conductivity relative to the electrolyte solution. This solution contains a UV-absorbing species and samples are detected by absorbance loss as they displace the buffer in the detector's light path. Careful maintenance of the electroosmotic flow rate, pH, and the age of the buffer solution are necessary to obtain reliability in this method. This technique helps confirm IC peaks by serving as a complement to it. It is more sensitive; a typical separation efficiency is 70,000 plates as opposed to 3,000 for IC. The cation standard was identical to the IC standard. The anion standard also included the carbonate anion.

Analysis of Anions by CIA

The anions present in all six of the powder extracts were nitrate and carbonate. Perchlorate was indicated in the extracts of Pyrodex^R, Black Mag, and Clean Shot.

Analysis of Cations by CIA

The cations found in the sample powders were much more consistent. Significant amounts of potassium, calcium, and sodium ions were found in all of the extracts along with a smaller amount of magnesium. The fact that the potassium peaks were the largest is not surprising since potassium nitrate is the primary oxidizer in each.

Comparison of IC, ICA, and Spot Test Results

According to the analyses listed above and Appendix I, the major anionic and cationic species in the extracts of the powders and residues are listed below:

Table 5. Major anionic and cationic species in intact powders

	ANIONS	CATIONS
Black Powder	Nitrate, sulfate	Sodium, potassium, calcium
Pyrodex	Nitrate, sulfate, perchlorate	Sodium, potassium, calcium
Black Canyon	Nitrate	Sodium, potassium, calcium
Golden Powder	Nitrate	Sodium, potassium, calcium
Black Mag	Nitrate, perchlorate	Sodium, potassium, calcium
Clean Shot	Nitrate, perchlorate	Sodium, potassium, calcium

Table 6. Major anionic and cationic species in residue powders

	ANIONS	CATIONS
Black Powder	Nitrite, nitrate, thiocyante, sulfate	Sodium, potassium
Pyrodex	Chloride, nitrite, sulfate, chlorate, thiocyanate, perchlorate	Sodium, potassium, calcium, ammonium
Black Canyon	Nitrite, nitrate	Sodium, potassium, ammonium
Golden Powder	Nitrate, nitrate	Sodium, potassium, ammonium
Black Mag	Chloride, nitrite, nitrate, chlorate, perchlorate	Sodium, potassium, calcium
Clean Shot	Chloride, nitrite, nitrate, chlorate, thiocyanate, perchlorate	Sodium, potassium, calcium, ammonium

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High Performance Liquid Chromatography Analysis

Although black powder, Pyrodex^R, and black powder substitutes share some common chemical components, Pyrodex^R also contains sodium benzoate and dicyandiamide.[29] It is much easier to differentiate between residues if unique species are present in a powder. After applying every powder, both extract and residue, to the appropriate solvent system and method to detect benzoic acid and DCDA, Pyrodex^R remained the only powder of the six to contain these two chemical species. Please refer to Appendix V for relevant data.

Discussion

X-ray Diffraction

Due to the almost unique crystalline structure of materials, identifying materials by the shape of their crystals is a useful method. The external shape of a crystal is a reflection of its interior and the external faces of the crystal are parallel to the lattice planes. The lattice planes are characteristic of a crystal. The powder diffraction method involves X-ray beams striking the crystal whose lattice planes then diffract the beam and produce a line. From this line, corresponding interplanar spacings are calculated. The spacings calculated from the three most intense lines are then used to identify the crystal and its materials.[21] Although similar crystal patterns may appear, the actual components of the crystal influence the intensities of the lines of the powder pattern. Identification of these materials involves recognizing their patterns.

X-ray diffraction offers several advantages. Unlike chromatography methods that reveal the ions present, x-ray diffraction reveals their combinations; it will identify the compounds in a sample. It is also capable of differentiating between several crystalline forms of the same compound as well as identifying various hydrates. Second, the method is non-destructive and requires only a small sample volume for accurate and rapid results.

However, there are correlating disadvantages as well. The sample must be in the powdered form. Although sometimes this involves only crushing a solid sample, other times this may involve an attempt to recover a solution, which is a tenuous situation in many instances. Additionally, if a material represents only a few percent of the total sample, its presence may not be recorded. Finally, the materials in the sample will only be identified if the known material is included in the database searched by the software used for analysis.

The x-ray diffraction patterns were measured from five degrees to sixty degrees in increments of 0.02. The analysis and identification of the peaks were completed using JADE for Windows software.[30] This software uses powerful computerized techniques to automatically find and characterize peaks. All samples were searched for inorganic peaks first. If peaks remained, a search of organic materials ensued.

Black powder revealed the compounds it is known to contain, i.e. potassium nitrate and sulfur. The charcoal does not have a crystalline form and is therefore not observed. This x-ray pattern has remained relatively unchanged for over 100 years.[31] Pyrodex^R also revealed no surprises in its composition. Like black powder, it contains potassium nitrate and smaller amounts of sulfur. It also contains the stabilizer sodium benzoate and the additional oxidizer potassium perchlorate.[9]

Because one objective of black powder substitutes may be to remove sulfur and its disagreeable effects, it was no surprise that none of the diffraction patterns of four of the substitute powders revealed the presence of sulfur. Golden Powder, Black Canyon, Black Mag, and Clean Shot Powder all contained potassium nitrate and ascorbic acid.

Ascorbic acid, $C_6H_8O_6$, or Vitamin C, has known antioxidant and food preservative properties. In the past ten years, ascorbic acid has also been studied as an additive in explosive compositions. Since it is less susceptible to ignition by friction and can sustain pressure for higher periods of time, compositions that contain it are only classified as flammable solids.[32] When combined with sources of nitrate, these compositions have been observed to function as gunpowder substitutes, explosives, and propellants. The products are stable in air and do not detonate easily, if at all. As a powder, they can be used in propellant applications or as a viable black powder substitute. In replacing sulfur as an additional fuel, the presence of ascorbic acid appears to lower both the corrosivity upon contact with metal and smoke evolution. Compared to known explosive powders, these substitute powders have a higher explosive power, distinctly lower hygroscopicity, and better stability.[10] Additionally, the absence of sulfur leads to less fouling and less emission of its characteristic distasteful odor.

The composition of Black Mag and Clean Shot Powder also include potassium perchlorate. One of the major claims stated explicitly in the Pyrodex^R patent is that it is safer to handle.[9] This additional safety comes from a slightly higher ignition point that may be the result of the potassium perchlorate. Since the alkali metal perchlorates themselves are readily available, inexpensive, stable, and safe to handle, it is justifiable to extend this claim to the materials in which they are included, such as Pyrodex^R and the black powder substitutes incorporating perchlorate.

There are numerous patents on substitute black powder compositions that include potassium perchlorate and/or ascorbic acid. One patent limits the amount of potassium perchlorate to between 6 and 15 percent while not limiting the amount of ascorbic acid.[11] Another patent's limits only dictate the presence of an inorganic nitrate and ascorbic acid with percentages of 50 to 75 and 25 to 50 respectively.[10] It is therefore no surprise the x-ray diffraction revealed compositions that included the same materials mentioned in the patents. Whereas Black Mag and Clean Shot Powder both contain the same components, the difference lies in the percentages of each and their corresponding ratios. However, since no quantitative studies were undertaken in this project, no estimates can be offered as to the approximate percentages of each component in a specific powder. Due to the scant product and manufacturing information, future quantitative studies determining exact concentrations of materials would be beneficial.

Spot Tests

Spot tests are qualitative analyses used to identify components of a sample. When a specific reaction occurs, a spot test is capable of indicating the presence of a certain element even in the presence of a large excess of other substances. Although spot tests make no claims to uncover the percent composition or molecular weight of an unknown material, they are often capable of revealing physical and chemical properties, the presence of functional groups, and general classes of substances.[23]

In simplest terms, a drop of the test solution is mixed with a drop of the liquid, or infrequently, solid reagent. This addition then provokes a physical, observable reaction. In terms of material and time, spot tests require only minimum levels of both. The levels of detection are inherently small but due to a distinct possibility of interfering elements, they sometimes provide false information. Thus, being absolutely certain of the identity of an element in the presence of large amounts of other materials is not impossible, but it is indeed rare.[23] However, spot tests do serve as an important preliminary technique for anion and cation detection that can be confirmed by further analysis.

In this project, they were performed first in the scheme of analysis on the liquid extracts and residues. The results were assumptions and only confirmed by further chromatographic methods. As tests yielding purely preliminary results, the spot tests were indeed accurate in the sense that they were confirmed by other methods as will be discussed later.

All of the powder extracts produced the deep red ring indicative of a positive result for the nitrate spot test, or Modified Greiss Test. However, when performing the Greiss Test on the residues, the results sometimes interfered with the Modified Greiss Test on the residues. The ring forming around the zinc powder could not always be observed due to the deep red color already present from the Greiss test for nitrites. When this interference happened, no result could be observed and N/A was recorded. This problem occurred only with the residues since they contain high amounts of nitrites and much decreased levels of nitrates compared to the original formulation. When this problem is encountered, both the nitrite ion and excess azide can be removed; sodium azide under acidic conditions decomposes the nitrite ion and heating the sample to near boiling removes the excess azide. Although it is highly probably that the residues in which the interference occurred did contain smaller amounts of nitrates due to powder that remained intact after combustion, they cannot alone characterize low explosive residue.[8] Thus, further removal was not completed and seen as unnecessary.

Originally, two tests for perchlorate were performed that involved methylene blue. The results of the spot test were easily observed. However, the microcrystal test was more difficult to perform and observe. Therefore, only the methylene blue spot test was used on subsequent samples.[23] Black Mag, Clean Shot, and Pyrodex^R showed positive results with the perchlorate spot test by fading to a lighter blue and forming a dark precipitate after a period of time.

The positive results for the residues were more varied. Since perchlorate is more concentrated in the intact powder before combustion, results were harder to determine in the residues. Of the powders that contain perchlorate, the residues of Pyrodex^R and Black Mag had slight positive results. The residue for Clean Shot powder, whose composition includes perchlorate, had a negative result. The amount of perchlorate left after combustion must have been below the level of detection for the spot test, which is approximately 500 ppm.[23] This illustration of the problem with levels of detection for spot tests is definitely incentive to use them only as a preliminary technique in a scheme of analysis.

The chloride spot test produced turbidity, which is indicative of a positive result, only in the residues of the powders containing perchlorate, i.e. Pyrodex^R, Black Mag, and Clean Shot powder. The thiocyanate spot test was only positive for samples that included sulfur in their composition; a rose color developed in the residues of black powder and Pyrodex^R.

The test for oxidizers is a general screening technique for oxidative species such as NO_2^-, NO_3^-, and ClO_3^-. The permanent ultramarine color indicative of the presence of nitrate was never observed. The blue color that does not fade and is indicative of chlorate

was observed only with the Black Mag Residue. The remainder of the positive results, the residues of the other five powders, turned blue and then faded to a yellow-green color. This coloration is indicative of the presence of nitrite. It is highly possible that the other samples that include perchlorate in their composition could also include chlorate; chlorate is one of the combustion products of perchlorate.

The sulfide spot test is the only test that could not be confirmed by further analysis. Thus, its results were record only as a possibility of being present. This test was only positive for the residues of Pyrodex^R and black powder. Since these two powders do contain sulfur, sulfide is a likely combustion product. However, their presence cannot be confirmed unless a sulfide standard is included in IC or CIA analysis in the future.

The sulfur spot test was completed to see if any sulfur could be detected in low part per million quantities. A positive result would negate the manufacturer's claims that their products contain no sulfur. The negative results for the residues of Golden Powder, Black Canyon, and Clear Shot, however, reveal that there is no detectable sulfur in the chemical compositions of these powders. However, the dark material left on the filter paper after the sulfur was removed is indicative of charcoal. It is likely that a small amount of charcoal is used in these substitute powders as an additional fuel, complementing ascorbic acid.

Chromatographic Methods

Major criteria for effective chromatographic analysis is the ability of the method to separate the species of interest, to reproduce retention times, and to minimize interferences. For many years, ion chromatography (IC) has been employed by the

forensic chemist to determine the ionic species in explosive residues.[1,33,34] Since explosive residues are water soluble, IC is an efficient technique. Employing ion exchange resins, IC has a well-known ability to provide excellent separations of ionic species. Developed in the early 1970s, the high sensitivity and qualitative accuracy of IC led to many applications. One such application involved its adaptation for the analysis of ions of interest in explosive scenes. In 1975, Small, Stevens, and Bauman solved the problem of neutralizing the conductivity of the background electrolyte.[25] By employing a combination of resins that neutralize these background ions, the sample ions are left as the only major conducting species in the effluent. In 1980, it was implemented in the FBI laboratory.[34] The ATF followed suit several years later. With the number of pipe bomb cases exploding, IC has become an important tool for analyzing these residues.

Both anion and cation analysis were completed on the intact powder and their residues. The ATF recently formulated both the anion and cation systems to be isocractic systems. Since an isocratic system is inherently easier to run than a gradient system, run times and operational problems were reduced. With the installation of autosamplers, the analyses became even less tedious. After preparing the eluent and preparing the samples, the autosampler takes care of the injection. For both cation and anion analysis, two standards were run in between two water blanks. Water blanks were also run in between each individual sample. In each instance that either the anion or cation systems were run, the water blanks indicated no contamination before, after, or in between samples

Although initially it took up to an hour to settle the conductivity into an appropriate range, neither the conductivity nor the pump created any problems during the actual cation and anion analysis. The cation analysis did not reveal anything discerning.[35] Every sample, both intact powder and residue, contained potassium and sodium in relatively large amounts. Smaller amounts of calcium and ammonium were found in almost all of the samples as well. It is worthy to note that the calcium in the extracts of Clean Shot and Black Mag were in a much higher quantity than the other powders. In fact, the existence of calcium in the extracts and residues of black powder, Pyrodex[R], Golden powder, and Black Canyon powder could not be considered significant. The high amount of potassium can be contributed to the major ingredient, potassium nitrate, in each of the samples. The sodium and calcium present in each sample is harder to explain. Their existence can only be a conjecture. Their most likely source is as an environmental contaminant. However, if a manufacturer is able to obtain contaminated potassium nitrate that is cheaper and functions equally or with no significant disadvantage to a pure lot, then the contaminated lot may be used. Since an efficient business operates under the precepts of price and availability, the lots contaminated with calcium and sodium may indeed be prevalent. Although sodium nitrate has a greater hydroscopicity and oxidizer containment, its presence has been noted in black powder compositions.[35]

The presence of the ammonium ion in the Pyrodex[R], Black Canyon, Clear Shot, and Golden Powder residues can only be a conjecture as well. Earlier research that revealed the ammonium ion attributes its existence to soil contamination.[35] Although that is not the case in this particular study, it is a verifiable conclusion. Instead, it is more likely that ammonium nitrate could have been substituted for potassium nitrate to some degree. Another speculation involves its existence as a reduction product of nitrite that appears after combustion. Since ascorbic acid is a strong reducing agent, it is possible

that the nitrate was reduced to ammonium, which would involve a transfer of three electrons. If this reduction process was the explanation, further qualitative tests need to be performed to see if there is a specific ratio formulation for the different chemical species in the powders that enhance the reduction process. Further studies would also be beneficial in order to determine if the ammonium nitrate is characteristic of the powder in general or of the specific lot used in this study.

The anion analysis and interpretation involved more species of interest. The extracts were relatively simple. The major identified anionic species in the extracts of black powder, Golden Powder, and Black Canyon was nitrate. These results agreed with earlier published work on black powder and Golden Powder.[36] This nitrate obviously was due to the potassium nitrate in their compositions. The major identified anionic species in the extracts of Pyrodex^{R}, Black Mag, and Clean Shot Powder were nitrate and perchlorate. The nitrate was again from the potassium nitrate while the perchlorate was from the potassium perchlorate in their compositions. Finally, chloride was also present in Pyrodex^{R}, Black Mag, and Clean Shot Powder in low levels. Chloride is a minor by-product in the commercial production of perchlorate.

However, the residues of the powders provided greater variation. Significant amounts of nitrite were found in each residue due to the reduction of nitrate upon combustion.[37] Smaller amounts of nitrate not affected by reduction were evident as well in the residues. The three sample powders that have potassium perchlorate, i.e. Pyrodex^{R}, Black Mag, and Clean Shot Powder, had slight traces of perchlorate left over in their residues. However, perchlorate undergoes a reduction when combusted.

Below is the characteristic reaction equation.

$$ClO_4^- \longrightarrow ClO_3^- \longrightarrow Cl^-$$

The most significant peaks were those of chloride, which is the main reduction product of perchlorate.[37] To a lesser extent, chlorate peaks were observed in the residues as well. Finally, due to the sulfur content in black powder and Pyrodex^R, these species also included the sulfate and thiocyanate ions in their residues.

One interpretation problem was apparent in the residues. In each of the substitute black powder residues, there is a tiny trace of the sulfate ion. The sulfate ion is understandable in the residues of black powder and Pyrodex^R because their compositions contain sulfur and thus the peak is of a significant size. Alternately, the size of the sulfate peaks in the substitute powders is insignificant when compared to the size of the sulfate peaks in black powder and Pyrodex^R.

The presence of a sulfate peak in the substitute powders is puzzling. One very hypothetical explanation could be attributed to the charcoal that was evidenced by black material remaining on the filter paper after the sulfur spot test. Perhaps this charcoal was wood charcoal containing a small of sulfur. Whatever the case, it is important to note that the sulfate was only picked up by the IC, which has an extremely high level of detection. The sulfur was not in a high enough concentration to be detected by either the sulfate or sulfur spot test. Thus, the miniscule amount of sulfur detected is not a major species in the black powder substitute compositions in any way.

Another possible explanation involves the instrumentation itself. The only species the IC detects are those that are present in the standard. It is therefore possible that there is a species that elutes around the same time as sulfate but is not sulfate.

Further tests would be needed to determine if there is an additional species and its identity. As evidenced by earlier discussion, it is very difficult to manufacture a mass-market gunpowder product completely free of contaminants and minor species.

There were also slight traces of chloride in the Black Canyon and Golden Powder residues. Although they do not contain potassium perchlorate and the presence of chloride cannot be attributed to the reduction products of it, chloride is a widespread environmental contaminant. It is on streets, on walls, and other obvious places inhabited by human beings and their daily efforts. This, of course, includes the forensic laboratory in which these tests were conducted.

No sample powder had significantly different IC results than those of other powders. However, the presence of perchlorate in Black Mag and Clean Shot Powder does differentiate them from Black Canyon and Golden Powder. Black Powder and Pyrodex^R can be differentiated from all four of the substitute black powders due to the presence of significant sulfate and thiocyanate peaks. Obviously, black powder substitute manufacturers are most concerned with eliminating the sulfur and its ensuing problems from their products.

The second chromatographic, or separation, method used was capillary ion analysis. This is a variation of capillary electrophoresis. As an analytical method, it is rapid, simple, and has the potential for excellent separation. In general, the principle of capillary electrophoresis involves applying voltage to cause differential migration of charged sample components.[38] These separated analytes are then passed through a detector. Several factors influence electrophoretic separation including size, shape, charge, mass, and interaction with the carrier electrolyte. The overall mobility is also

influenced by electroosmotic mobility, which involves loosely charged cations associating with the negatively charged interior of the capillary wall.

To analyze ions with small molecular weights, capillary ion analysis is employed. In this method, analytes always migrate in the same direction as the electroosmotic flow (EOF). While cation analysis involves both an analyte and a pH-controlled EOF that travel in the same direction, anion analysis requires a reversal of the EOF by an electrolyte modifier that coats the inner wall of the capillary.[38] The preferred method of detection is by indirect ultraviolet (UV) detection.

Capillary ion electrophoresis is best viewed as a complementary technique to ion chromatography. Despite having shorter run times and a slightly heightened sensitivity, it is a much newer method. As such, it has not been as extensively studied or used in the field of forensic science. However, there is positive data when IC and CE are used in tandem for explosive residue analysis.[33] These two techniques were complementary in this project. The CE available at the ATF is newer than the IC and has not had much time or effort dedicated to its use. Melinda Ferguson, an intern at the ATF, was responsible for its upkeep and use. She delivered a talk at the end of her internship stating that not enough tests have been done on the CE to include it in routine explosive analysis. The major problem she encountered was co-elution, especially if the sample was too concentrated. Although the software facilitated the interpretation of the chromatograms, it contributed to the problem of co-eluted peaks.

For anion analysis, the samples were around 30 ppm and for cation analysis, the samples were around 10 ppm. With the time already devoted to learning and running the IC already, it was not efficient for me to learn the care and use of the CE. Since the data was only seen as complementary to IC and was not proof in itself of the presence of a certain ionic species, Melinda ran the prepared samples.

The cations present in the extracts of the six powders included significant amounts of potassium and sodium and less significant amounts of calcium and magnesium. The calcium was again more significant in the extracts of Black Mag and Clean Shot Powder. In general, these results were compatible with the results of the IC. However, the detection of magnesium is due to the more sensitive nature of the CIA. Only minute amounts of magnesium were found and are most likely attributed to environmental contamination that is not a major species in the sample composition.

The major anion present in the extract was nitrate. Pyrodex^R, Black Mag, and Clean Shot also contained perchlorate. These results are analogous to those obtained from the IC. For the same reasons as outlined above, these are the major anionic species that are expected to be detected in the powder samples.

After performing the two chromatographic methods IC and CIA, it indeed does seem that they are complementary in nature. There were no significant differences in the results for the powder extracts. Although CIA may seem faster as well as more sensitive and efficient, it is less thoroughly researched and cannot stand alone as an analytical confirmation. Additionally, the IC is a finicky instrument whose standards can be difficult to reproduce. Due to the inherent deficiencies in both, it is conducive to the scientist to perform both methods for confirmation purposes. Used in tandem, these two methods are capable of detecting the presence of the ions most characteristic of explosive materials.

High Performance Liquid Chromatography

Liquid chromatography is a separation technique that relies on specific interactions between the sample molecules and those of the stationary and mobile phases. This technique can be extremely advantageous. First, it is not limited by sample volatility or thermal stability. Second, it can achieve difficult separations due to its reliance on two chromatographic phases and low separation temperatures. Finally, there are an abundance of useful column packings, stationary phases, and detectors that are available and effective for this technique.[28]

One specific application of this technique is in the area of explosives. Reported in 1989 by Edward Bender of the Materials Analysis Unit in the FBI Laboratory, this application is specific in detecting the presence of Pyrodex^R.[29] By using specific solvents, optimum separation is achieved for two stabilizing materials. Besides potassium nitrate and potassium perchlorate, Pyrodex^R also contains sodium benzoate and dicyandiamide (DCDA). These two materials are unique to Pyrodex^R. Although black powder, Pyrodex^R, and the black powder substitutes look different before combustion, these differences become less significant after combustion. Thus, chemical analysis is required to characterize the residue. The process for detecting the two stabilizers mentioned above, sodium benzoate and DCDA, is capable of distinguishing Pyrodex^R residue from the residue of black powder and its substitutes. Therefore, the sensitivity and selectivity of this application of HPLC is important in determining the residues specific to Pyrodex^R.

When this application of HPLC was applied to the extracts of the six powders, only Pyrodex^R revealed the elution of two peaks at the times that are characteristic of benzoic acid and DCDA. No qualitative determination was undertaken, although previous work has been done to show that the concentration of sodium benzoate and DCDA in Pyrodex^R RS to be 6 and 12 percent respectively.[29]

In the residues, the two compounds again only appeared in Pyrodex^R. This result supports the earlier finding that these two compounds survive combustion. Sodium benzoate and DCDA continue to be evidence of the presence of Pyrodex^R since no black powder substitute shows evidence of their existence. However, this statement can only be generalized to include the four black powder substitutes tested in this study.

It is interesting to note that no other black powder substitute contains these stabilizers. One can only conjecture as to why their presence is not more ubiquitous in low explosive compositions. Pyrodex^R received its patent in 1978.[9] One stipulation of the patent is that it contain "approximately 14.5-45 parts by weight of an organic carboxylic acid or oxidizable derivative thereof...."[9] Further, it emphasizes the effectiveness of sodium benzoate in terms of cost, availability, and inhibition of corrosion and specifically claims:

> 1. In a deflagrating gas generation composition for producing controlled gas pressure which imparts high velocity to projectiles at relatively low peak pressure, the improvement which comprises employing, a the essential gas-producing elements, approximately 82.5-30 parts by weight of an oxidizing agent selected from the group consisting of ammounium, alkali metal, and alkaline earth nitrates, chlorates and perchlorates; approximately 14.5-45 parts by weight of an oxidizable derivative of an organic carboxylic acid selected from the group consisting of ammonium and alkali metal salts of aromatic carboxylic acids; and approximately 25-1.0 parts by weight of water.
> 6. A composition according to claim 1 which consists of from 20 to 50 percent of the composition claimed therein admixed with from 80 to 50 percent of the components of black powder.
> 7. A composition according to claim 6 which consists of 45 parts of potassium nitrate, 9 parts of charcoal, 6 parts of sulfur, 19 parts of potassium perchlorate, 11 parts of sodium benzoate, 6 parts of dicyandiamide and from 1 to 4 parts of water.[9]

Perhaps the limits that the patent sets on the amounts of sodium benzoate and dicyandiamide are the specific formulation needed for maximum effectiveness. Or pe

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perhaps it is in combination with the other mixture of materials specific to Pyrodex^R which necessitate the need for the added stability gained from the presence of these two materials. Whatever the case, sodium benzoate and DCDA remain characteristic of only Pyrodex^R in this study.

Conclusion

After extensive study on several analytical instruments, the chemical composition of the water extracts and combustion of residues of Black Canyon, Golden Powder, Black Canyon, and Clean Shot Powder have been determined. A referral to Appendix I-V allows the chemist to compare an unknown sample to known specimens of each powder using several analytical techniques. X-ray diffraction allows compounds in only the intact material to be compared while spot tests, IC, and CIA allow for the comparison of characteristic ions in the intact material and its residues.

Although this study did not discover an ionic species capable of differentiating black powder substitutes individually or collectively, several groupings can be made. The two major groups include those substitute compositions with perchlorate and those without. If the perchlorate ion is found either in the extract or residue, it is fair to say that the powder is not black powder, Black Canyon, or Golden Powder.

Black powder substitutes as a whole can be distinguished from black powder and Pyrodex^R by sulfur alone. It is fair to say that if sulfur or any of its combustion products such as thiocyanate and sulfate are present, it is not a black powder substitute tested in this study.

Alternately, ascorbic acid is only characteristic of black powder substitutes. However, since it does not seem to form any different ionic species, this observation is

only helpful if the intact powder is recovered. Perhaps further quantitative studies will reveal that its presence impacts the detected amount of a certain ion. Additionally, these studies could reveal a characterizing relationship between the amount of certain ions detected in the residues of black powder substitutes.

One final conclusion concerns nitrates and nitrites. The presence of nitrates in extracts and the presence of nitrites in residues are ubiquitous amongst the powders tested in this study. Nitrates are a powerful oxidizer whose effectiveness in black powder and Pyrodex^R has not been altered significantly in substitute compositions. Whether or not this is due to a lack of study on alternative oxidizers is not known.

The small amount of information available today on black powder substitutes is geared toward a shooting audience. Although sport shooting is a safe recreational activity, another more dangerous activity involving the use of black powder substitutes includes the creation of destructive devices such as pipe bombs. As the number of pipe bomb cases increase and black powder substitutes become more readily available on the market, forensic scientists may be faced with compositions other than those typical of black powder and Pyrodex^R. Consulting this study may help these professionals generate comparisons and conclusions. And perhaps the manufacturers of the black powder substitutes in this study and others not studied will become more liberal with necessary information on the composition of their products. A final compilation of their compositions as determined by this study is listed on the final, following pages.

Table 7. Intact composition of powders

Extracts	**Black Powder**	**Pyrodex**	**Black Canyon**
Intact Materials	Potassium, Nitrate, Sulfate	Potassium, Nitrate, Potassium Perchlorate, Sodium Benzoate	Ascorbic Acid, Potassium Nitrate
Anions	Nitrate	Nitrate Chlorate Perchlorate	Nitrate
Cations	Sodium Potassium Calcium	Sodium Potassium Calcium	Sodium Potassium Calcium

Extracts	**Golden Powder**	**Black Mag**	**Clean Shot**
Intact Materials	Ascorbic Acid, Potassium Nitrate	Ascorbic Acid, Potassium Nitrate, Potassium Perchlorate	Ascorbic Acid, Potassium Nitrate, Potassium Perchlorate
Anions	Nitrate	Nitrate Perchlorate	Nitrate Perchlorate
Cations	Sodium Potassium Calcium	Sodium Potassium Calcium	Sodium Potassium Calcium

Table 8. Residue composition of powders

Residues	**Black Powder**	**Pyrodex**	**Black Canyon**
Anions	Nitrite Nitrate Sulfate Thiocyanate	Chloride Nitrite Nitrate Chlorate Thiocyanate Perchlorate	Nitrite Nitrate
Cations	Sodium Potassium Calcium	Sodium Potassium Ammonium Calcium	Sodium Potassium Ammonium Calcium

Residues	**Golden Powder**	**Black Mag**	**Clean Shot**
Anions	Nitrite Nitrate	Chloride Nitrite Nitrate Perchlorate	Chloride Nitrite Nitrate Chlorate Perchlorate
Cations	Sodium Potassium Ammonium Calcium	Sodium Potassium Calcium	Sodium Potassium Ammonium Calcium

APPENDIX I

Analytical Results

Compilation of Analysis Results

Photographs

A

Ca

X-RAY DIFFRACTION RESULTS

	Black Powder	Pyrodex	Black Canyon	Golden Powder	Black Mag	Clean Shot
Ascorbic Acid			X	X	X	X
Potassium Nitrate	X	X	X	X	X	X
Potassium Perchlorate		X			X	X
Sodium Benzoate		X				
Sulfur	X	X				

ION CHROMATOGRAPHY RESULTS

Anions In Water Extract	Black Powder	Pyrodex	Black Canyon	Golden Powder	Black Mag	Clean Shot
Chloride- Cl						
Nitrite- NO2						
Nitrate- NO3	X	X	X	X	X	X
Chlorate- ClO3		X				
Sulfate- SO4						
Thiocyanate- SCN						
Perchlorate- ClO4		X			X	X
Cations In Water Extract						
Sodium- Na	X	X	X	X	X	X
Ammonium- NH4						
Potassium- K	X	X	X	X	X	X
Magnesium- Mg					x	
Calcium- Ca	x	x	x	x	X	X
Strontium- Sr						
Barium- Ba						
Anions In Residue						
Chloride- Cl		X		x	X	X
Nitrite- NO2	x	X	X	X	X	X
Nitrate- NO3	x	X	X	X	X	X
Chlorate- ClO3						x
Sulfate- SO4	X	X	x	x	x	
Thiocyanate- SCN	x	X				
Perchlorate- ClO4		x			X	X
Cations In Residue						
Sodium- Na	X	X	X	X	X	X
Ammonium- NH4		x	x			x
Potassium- K	X	X	X	X	X	X
Magnesium- Mg			X			x
Calcium- Ca	x	X	x	x	X	X
Strontium- Sr						
Barium- Ba						

CAPILLARY ION ANALYSIS RESULTS

Anions in Water Extract	Black Powder	Pyrodex	Black Canyon	Golden Powder	Black Mag	Clean Shot
Chloride- Cl						
Sulfate- SO4						
Nitrite- NO2						
Nitrate- NO3	X	X	X	X	X	X
Chlorate- ClO3						
Thiocyanate- SCN						
Perchlorate- ClO4		X			X	X
Carbonate- CO3	X	X	X	X	X	X

Cations in Water Extract						
Ammonium- NH4						
Potasium- K	X	X	X	X	X	X
Calcium- Ca	X	X	x	x	X	X
Sodium- Na	X	X	X	X	x	X
Magnesium- Mg	x	x	x	X	X	x
Strontium- Sr						
Barium- Ba						

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY RESULTS

Water Extracts	Black Powder	Pyrodex	Black Canyon	Golden Powder	Black Mag	Clean Shot
Dicyandiamine (DCDA)		X				
Benzoic Acid		X				
Residues						
Dicyandiamine (DCDA)		X				
Benzoic Acid		X				

SPOT TEST RESULTS

Water Extracts	Black Powder	Pyrodex	Black Canyon	Golden Powder	Black Mag	Clean Shot
Ammonium Ion	Neg	Neg	Neg	Neg	Neg	Neg
Chloride Ion	Neg	Neg	Neg	Neg	Neg	Neg
Nitrate Ion	Pos	Pos	Pos	Pos	Pos	Pos
Nitrite Ion	Neg	Neg	Neg	Neg	Neg	Neg
Oxidizer	Neg	Pos	Neg	Neg	Neg	Neg
Perchlorate Ion	Neg	Pos	Neg	Neg	Neg	Pos
Perchlorate Ion- Crystals	Neg	N/A	Neg	N/A	N/A	Pos
Sulfate Ion	Neg	Neg	Neg	Neg	Neg	Neg
Sulfide Ion	Neg	Neg	Neg	Neg	Neg	Neg
Thiocyanate Ion	Neg	Neg	Neg	Neg	Neg	Neg

Residues						
Ammonium Ion	Neg	Neg	Low Pos	Neg	Neg	Neg
Chloride Ion	Neg	Pos	Neg	Neg	Low Pos	Pos
Nitrate Ion	Pos	Pos	Low Pos	Pos	N/A	N/A
Nitrite Ion	Pos	Pos	Pos	Pos	Pos	Pos
Oxidizer	Pos	Pos	Pos	Pos	Pos	Pos
Perchlorate Ion	Neg	Low Pos	Neg	Neg	Low Pos	Neg
Perchlorate Ion- Crystals	N/A	N/A	N/A	N/A	N/A	N/A
Sulfate Ion	Pos	Pos	Neg	Neg	Neg	Neg
Sulfide Ion	Pos	Pos	Neg	Neg	N/A	Neg
Thiocyanate Ion	Pos	Pos	Neg	Neg	Neg	Neg

COMPILATION OF ANALYSIS RESULTS

Black Powder

Anions	IC Extract	CE Extract	Spot Tests	IC Residue	Spot Tests
Chloride- Cl					
Nitrite- NO2				x	X
Nitrate- NO3	X	X	X	x	X
Chlorate- ClO3					
Sulfate- SO4				X	X
Thiocyanate- SCN				x	x
Perchlorate- ClO4					

Cations	IC Extract	CE Extract	IC Residue
Sodium- Na	X	X	X
Ammonium- NH4			
Potassium- K	X	X	X
Magnesium- Mg		x	
Calcium- Ca	x	X	x
Strontium- Sr			
Barium- Ba			

Pyrodex

Anions	IC Extract	CE Extract	Spot Tests	IC Residue	Spot Tests
Chloride- Cl				X	X
Nitrite- NO2				X	X
Nitrate- NO3	X	X	X	X	X
Chlorate- ClO3	X		X		X
Sulfate- SO4				X	X
Thiocyanate- SCN				X	X
Perchlorate- ClO4	X	X	X	x	X

Cations	IC Extract	CE Extract	IC Residue
Sodium- Na	X	X	X
Ammonium- NH4			x
Potassium- K	X	X	X
Magnesium- Mg		x	
Calcium- Ca	x	X	x
Strontium- Sr			
Barium- Ba			

COMPILATION OF ANALYSIS RESULTS

Black Canyon

Anions	IC Extract	CE Extract	Spot Tests	IC Residue	Spot Tests
Chloride- Cl					
Nitrite- NO2				X	X
Nitrate- NO3	X	X	X	X	X
Chlorate- ClO3					
Sulfate- SO4				x	
Thiocyanate- SCN					
Perchlorate- ClO4					

Cations			
Sodium- Na	X	X	X
Ammonium- NH4			X
Potassium- K	X	X	X
Magnesium- Mg		x	x
Calcium- Ca	x	x	X
Strontium- Sr			
Barium- Ba			

Golden Powder

Anions	IC Extract	CE Extract	Spot Tests	IC Residue	Spot Tests
Chloride- Cl				x	
Nitrite- NO2				X	X
Nitrate- NO3	X	X	X	X	X
Chlorate- ClO3					
Sulfate- SO4				x	
Thiocyanate- SCN					
Perchlorate- ClO4					

Cations			
Sodium- Na	X	X	X
Ammonium- NH4			x
Potassium- K	X	X	X
Magnesium- Mg		x	
Calcium- Ca	x	x	x
Strontium- Sr			
Barium- Ba			

COMPILATION OF ANALYSIS RESULTS

Clean Shot

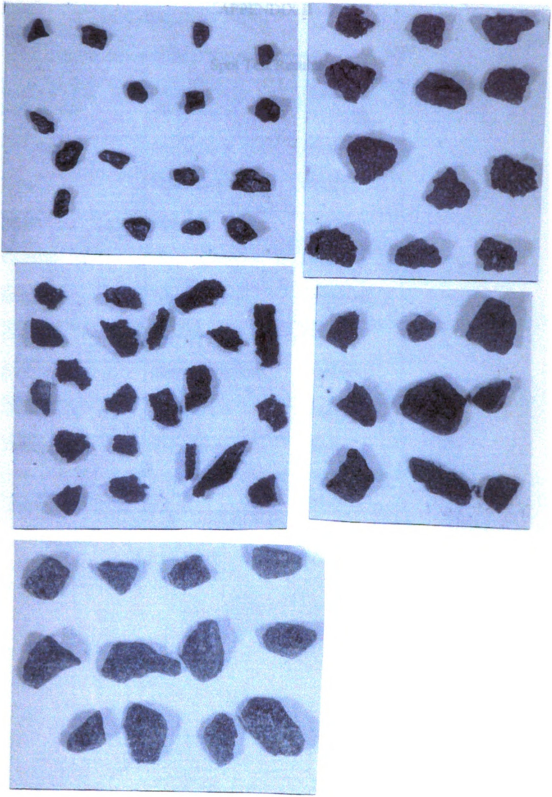
Anions	IC Extract	CE Extract	Spot Tests	IC Residue	Spot Tests
Chloride- Cl		x		X	X
Nitrite- NO2		x		X	X
Nitrate- NO3	X	X	X	X	X
Chlorate- ClO3				x	x
Sulfate- SO4					
Thiocyanate- SCN					
Perchlorate- ClO4	X	X	X	x	

Cations			
Sodium- Na	X	X	X
Ammonium- NH4		x	
Potassium- K	X	X	X
Magnesium- Mg		x	
Calcium- Ca	X	X	X
Strontium- Sr			
Barium- Ba			

Black Mag

Anions	IC Extract	CE Extract	Spot Tests	IC Residue	Spot Tests
Chloride- Cl				X	x
Nitrite- NO2				X	X
Nitrate- NO3	X	X	X	X	X
Chlorate- ClO3					X
Sulfate- SO4				x	
Thiocyanate- SCN					
Perchlorate- ClO4	x	X	X	x	x

Cations			
Sodium- Na	X	X	X
Ammonium- NH4			
Potassium- K	X	X	X
Magnesium- Mg	x	x	
Calcium- Ca	X	X	X
Strontium- Sr			
Barium- Ba			



From left to right starting in top row: **Goex Black Powder FFFG, Pyrodex RS, Golden Powder, Black Canyon Powder, Clean Shot Powder**

APPENDIX II

Spot Test Results

Chemical Spot Tests

Powder Name: ***Black Powder Extract***

Ion/Test Type	Observations	Result
Ammonium	*Pale Yellow*	*Negative*
Chloride	*No turbidity*	*Negative*
Nitrate	*Rose Ring*	*Positive*
Nitrite	*Brown*	*Negative*
Oxidizer	*No change*	*Negative*
Chlorate	*No change*	*Negative*
Chlorate	*No crystals*	*Negative*
Sulfate	*Slow precipitate*	*Positive*
Sulfur	*No change*	*Negative*
Thiocyanate	*Turns orange*	*Negative*

Analyst: JMY **Date:** 7/22/99

Chemical Spot Tests

Powder Name: ***Black Powder Residue***

Ion/Test Type	Observations	Result
Ammonium	*No change*	*Negative*
Chloride	*Dark, no precipitate*	*Negative*
Nitrate	*Rose Ring*	*Positive*
Nitrite	*Rose*	*Positive*
Oxidizer	*Blue, fade to yellow-green*	*Positive*
Chlorate	*Slight change*	*Negative*
Sulfate	*Slow precipitate*	*Positive*
Sulfur	*Dark, no precipitate*	*Positive*
Thiocyanate	*Darker*	*Low positive*

Analyst: JMY

Date: 7/22/99

<u>*Chemical Spot Tests*</u>

Powder Name: ***Pyrodex Extract***

Ion/Test Type	Observations	Result
Ammonium	*Pale Yellow*	*Negative*
Chloride	*No change*	*Negative*
Nitrate	*Rose Ring*	*Positive*
Nitrite	*Brown*	*Negative*
Oxidizer	*Blue fade to light yellow*	*Positive*
Chlorate	*Fades, precipitate*	*Positive*
Sulfate	*Slow precipitate*	*Positive*
Sulfur	*No change*	*Negative*
Thiocyanate	*Stayed yellow*	*Negative*

Analyst: JMY **Date:** 7/22/99

Chemical Spot Tests

Powder Name: ***Pyrodex Residue***

Ion/Test Type	Observations	Result
Ammonium	*No change*	*Negative*
Chloride	*Dark precipitate*	*Positive*
Nitrate	*Rose Ring*	*Positive*
Nitrite	*Rose*	*Positive*
Oxidizer	*Blue fades to yellow-green*	*Positive*
Chlorate	*Fade slightly*	*Low positive*
Sulfate	*Slow precipitate*	*Positive*
Sulfur	*Dark, precipitate*	*Positive*
Thiocyanate	*Red color*	*Positive*

Analyst: JMY

Date: 7/22/99

Chemical Spot Tests

Powder Name: ***Black Canyon Extract***

Ion/Test Type	Observations	Result
Ammonium	*Brown, muddy*	*Negative*
Chloride	*No change*	*Negative*
Nitrate	*Rose Ring*	*Positive*
Nitrite	*Brown*	*Negative*
Oxidizer	*No change*	*Negative*
Chlorate	*No change*	*Negative*
Chlorate	*No crystals*	*Negative*
Sulfate	*No change*	*Negative*
Sulfur	*No change*	*Negative*
Thiocyanate	*No change*	*Negative*

Analyst: JMY

Date: 7/27/99

Chemical Spot Tests

Powder Name: ***Black Canyon Residue***

Ion/Test Type	Observations	Result
Ammonium	*Darker, precipitate*	*Positive*
Chloride	*No change*	*Negative*
Nitrate	*Rose Ring*	*Low positive*
Nitrite	*Rose*	*Positive*
Oxidizer	*Blue fades to yellow-green*	*Positive*
Chlorate	*No change*	*Negative*
Sulfate	*No change*	*Negative*
Sulfur	*No change*	*Negative*
Thiocyanate	*No change*	*Negative*

Analyst: JMY **Date:** 7/27/99

Chemical Spot Tests

Powder Name: ***Golden Powder Extract***

Ion/Test Type	Observations	Result
Ammonium	*Darker*	*Negative*
Chloride	*No change*	*Negative*
Nitrate	*Rose Ring*	*Positive*
Nitrite	*Brown*	*Negative*
Oxidizer	*No change*	*Negative*
Chlorate	*No change*	*Negative*
Sulfate	*No change*	*Negative*
Sulfur	*No change*	*Negative*
Thiocyanate	*No change*	*Negative*

Analyst: JMY

Date: 7/27/99

Chemical Spot Tests

Powder Name: ***Golden Powder Residue***

Ion/Test Type	Observations	Result
Ammonium	*No change*	*Negative*
Chloride	*No change*	*Negative*
Nitrate	*Rose Ring*	*Positive*
Nitrite	*Rose*	*Positive*
Oxidizer	*Blue fades to yellow-green*	*Positive*
Chlorate	*Slight change*	*Negative*
Sulfate	*No change*	*Negative*
Sulfur	*No change*	*Negative*
Thiocyanate	*No change*	*Negative*

Analyst: JMY **Date:** 7/27/99

Chemical Spot Tests

Powder Name: ***Black Mag Extract***

Ion/Test Type	Observations	Result
Ammonium	*No change*	*Negative*
Chloride	*No change*	*Negative*
Nitrate	*Rose Ring*	*Positive*
Nitrite	*No change*	*Negative*
Oxidizer	*No change*	*Negative*
Chlorate	*No change*	*Negative*
Sulfate	*No change*	*Negatvie*
Sulfur	*No change*	*Negative*
Thiocyanate	*No change*	*Negative*

Analyst: JMY **Date:** 7/27/99

Chemical Spot Tests

Powder Name: ***Black Mag Residue***

Ion/Test Type	Observations	Result
Ammonium	*No change*	*Negative*
Chloride	*Turbidity*	*Low positive*
Nitrate	*Too dark to tell*	*N/A*
Nitrite	*Deep red*	*Positive*
Oxidizer	*Deep blue*	*Positive*
Chlorate	*Slight change*	*Low positive*
Sulfate	*No change*	*Negative*
Sulfur	*Dark precipitate with heat*	*N/A*
Thiocyanate	*No change*	*Negative*

Analyst: JMY

Date: 7/27/99

Chemical Spot Tests

Powder Name: ***Clean Shot Extract***

Ion/Test Type	Observations	Result
Ammonium	*Darker*	*Negative*
Chloride	*No change*	*Negative*
Nitrate	*Rose Ring*	*Positive*
Nitrite	*Brown*	*Negative*
Oxidizer	*No change*	*Negative*
Chlorate	*Lavendar needles*	*Positive*
Chlorate	*White precipitate*	*Positive*
Chlorate	*White precipitate*	*Positive*
Sulfate	*No change*	*Negative*
Sulfur	*No change*	*Negative*
Thiocyanate	*No change*	*Negative*

Analyst: JMY **Date:** 7/22/99

Chemical Spot Tests

Powder Name: ***Clean Shot Residue***

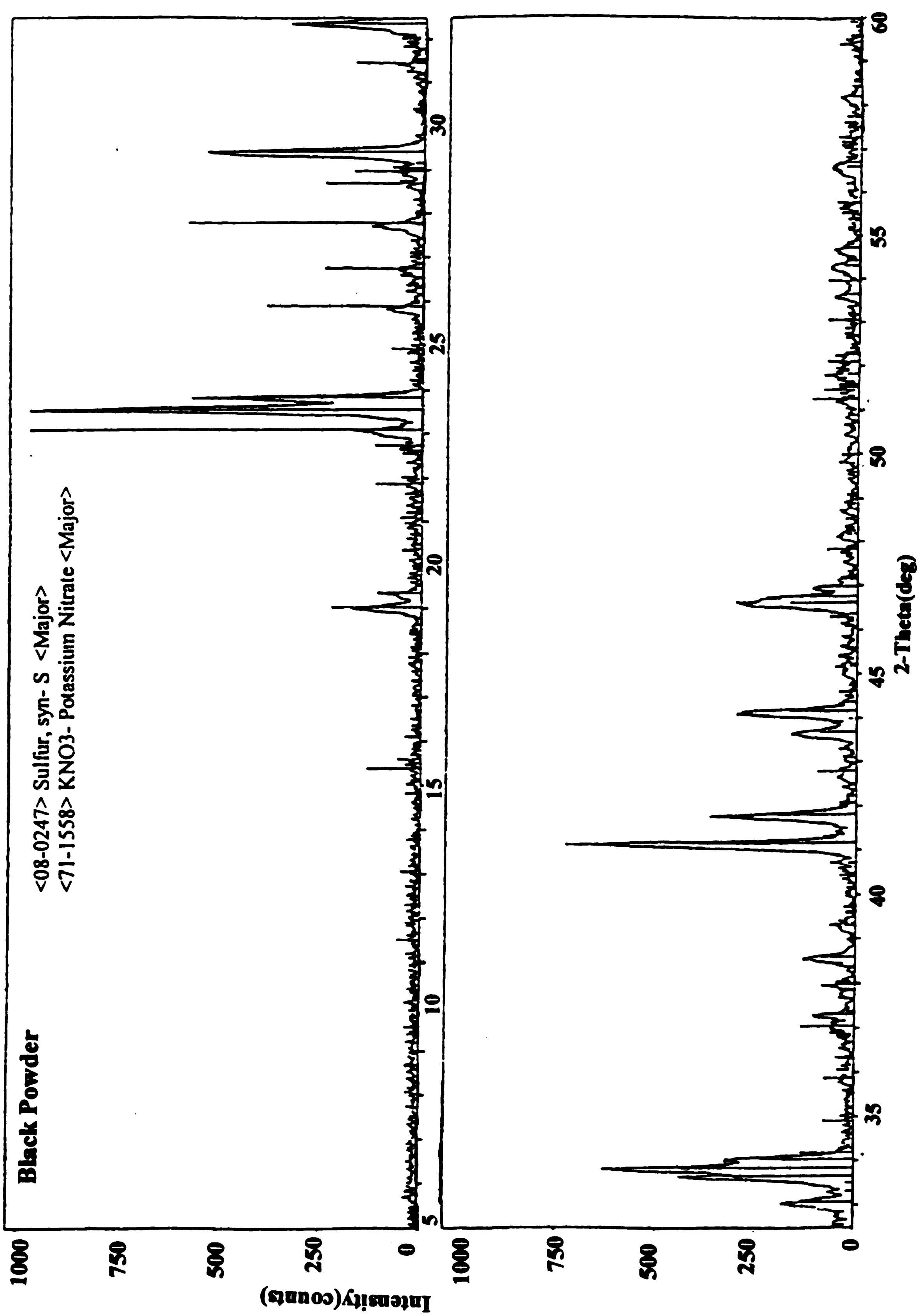
Ion/Test Type	Observations	Result
Ammonium	*No change*	*Negative*
Chloride	*Brown precipitate, white ppt with heat*	*Positive*
Nitrate	*Too dark to tell*	*N/A*
Nitrite	*Rose*	*Positive*
Oxidizer	*Blue fades to yellow-green*	*Positive*
Chlorate	*No change*	*Negative*
Sulfate	*No change*	*Negative*
Sulfur	*No change*	*Negative*
Thiocyanate	*Darker*	*Negative*

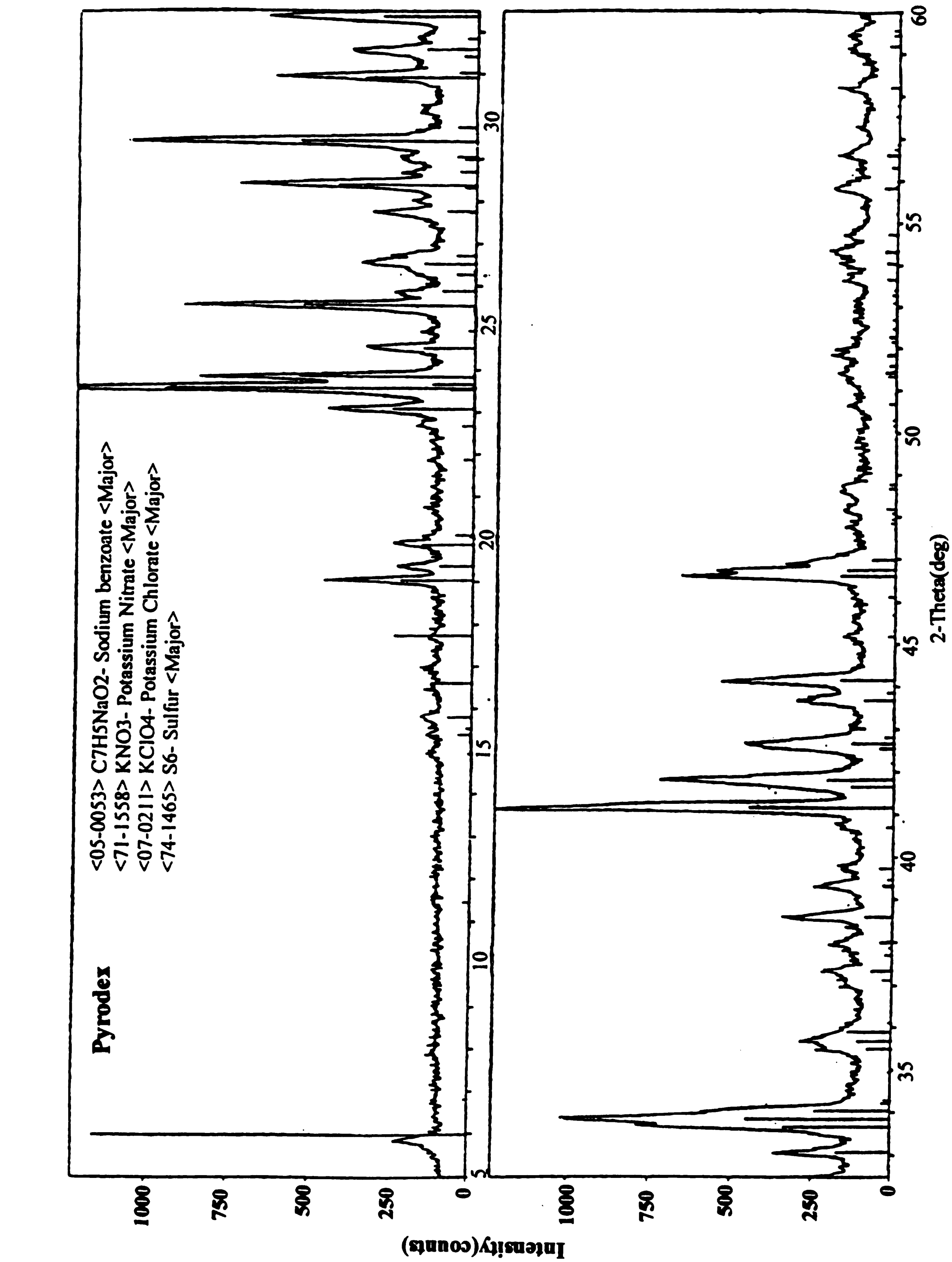
Analyst: JMY

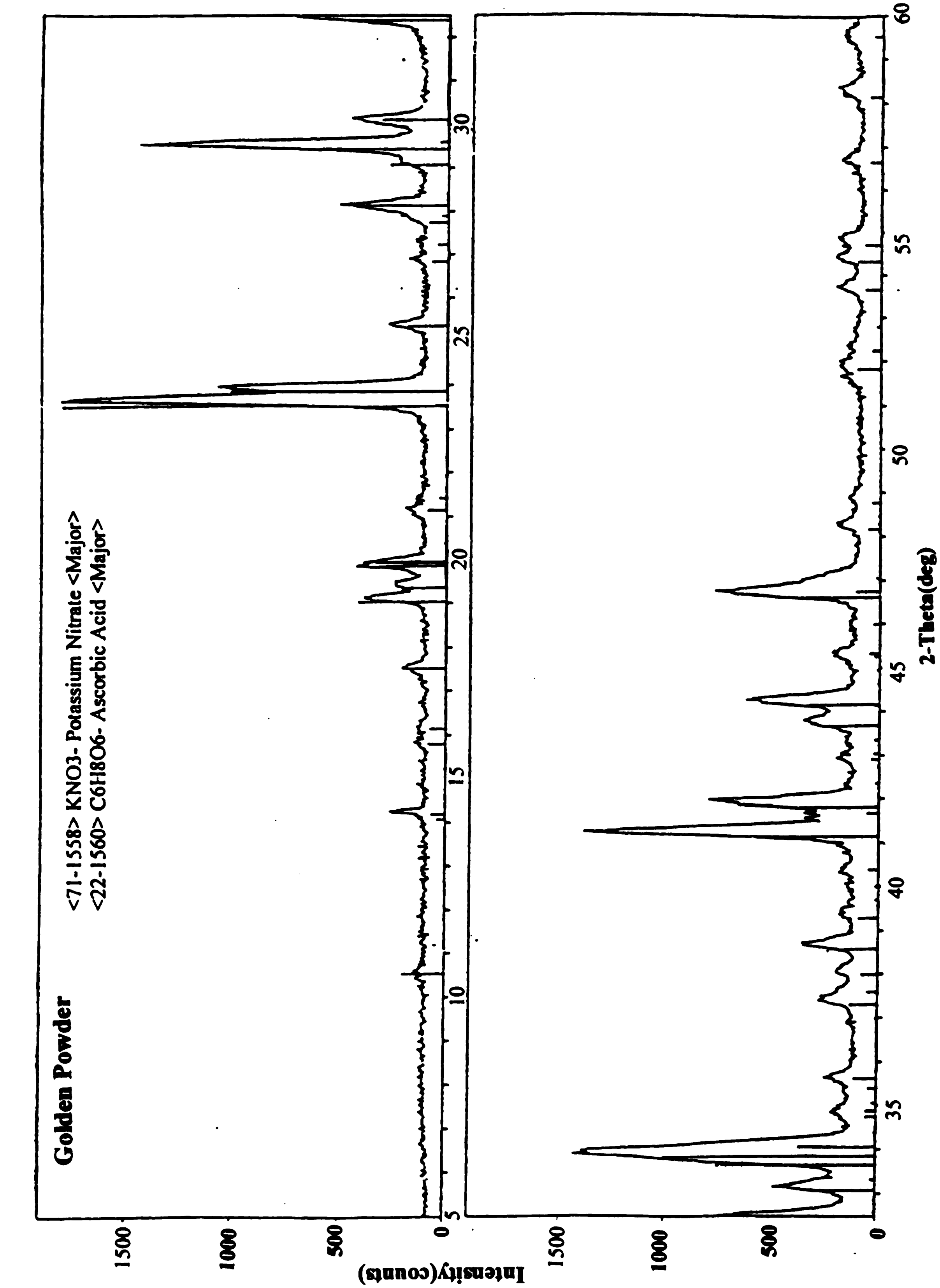
Date: 7/27/99

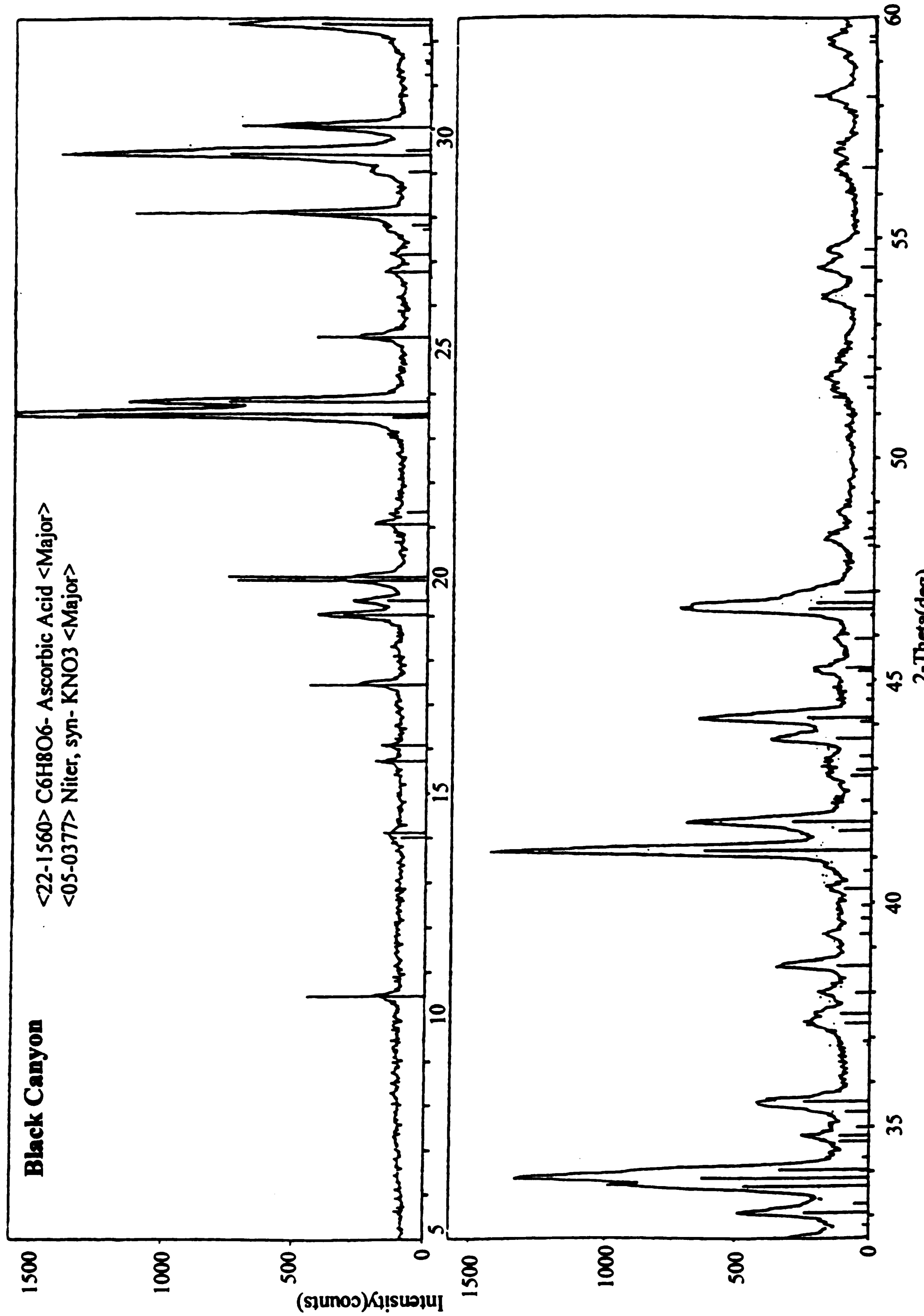
APPENDIX III

XRD Results

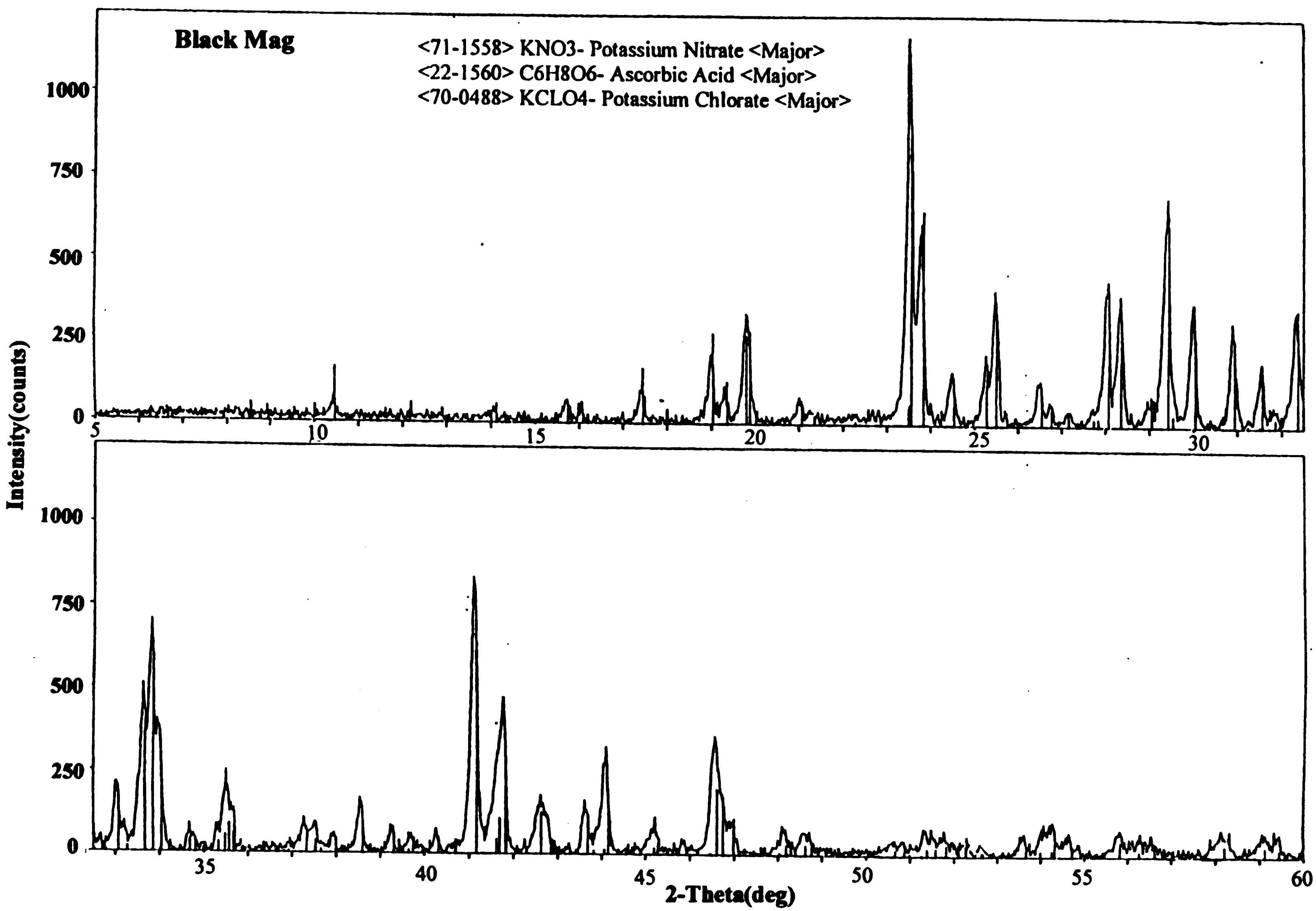

Black Powder
<08-0247> Sulfur, syn- S <Major>
<71-1558> KNO3- Potassium Nitrate <Major>
Intensity(counts)
1000
750
500
250
0
5
10
15
20
25
30
35
40
45
50
55
60
2-Theta(deg)

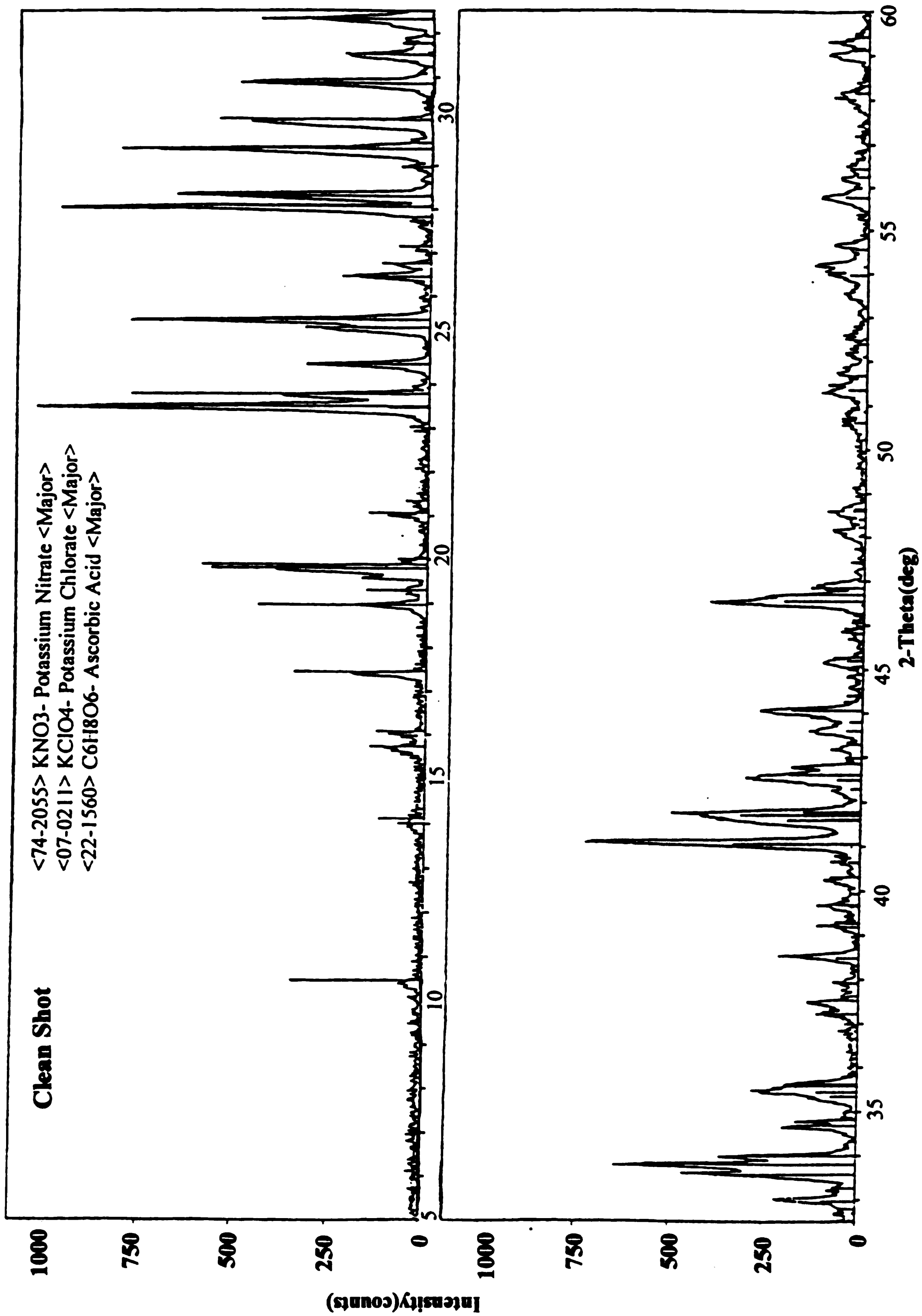

Pyrodex
<05-0053> C7H5NaO2- Sodium benzoate <Major>
<71-1558> KNO3- Potassium Nitrate <Major>
<07-0211> KClO4- Potassium Chlorate <Major>
<74-1465> S6- Sulfur <Major>
Intensity(counts)
2-Theta(deg)


Golden Powder
<71-1558> KNO3- Potassium Nitrate <Major>
<22-1560> C6H8O6- Ascorbic Acid <Major>
Intensity(counts)
2-Theta(deg)



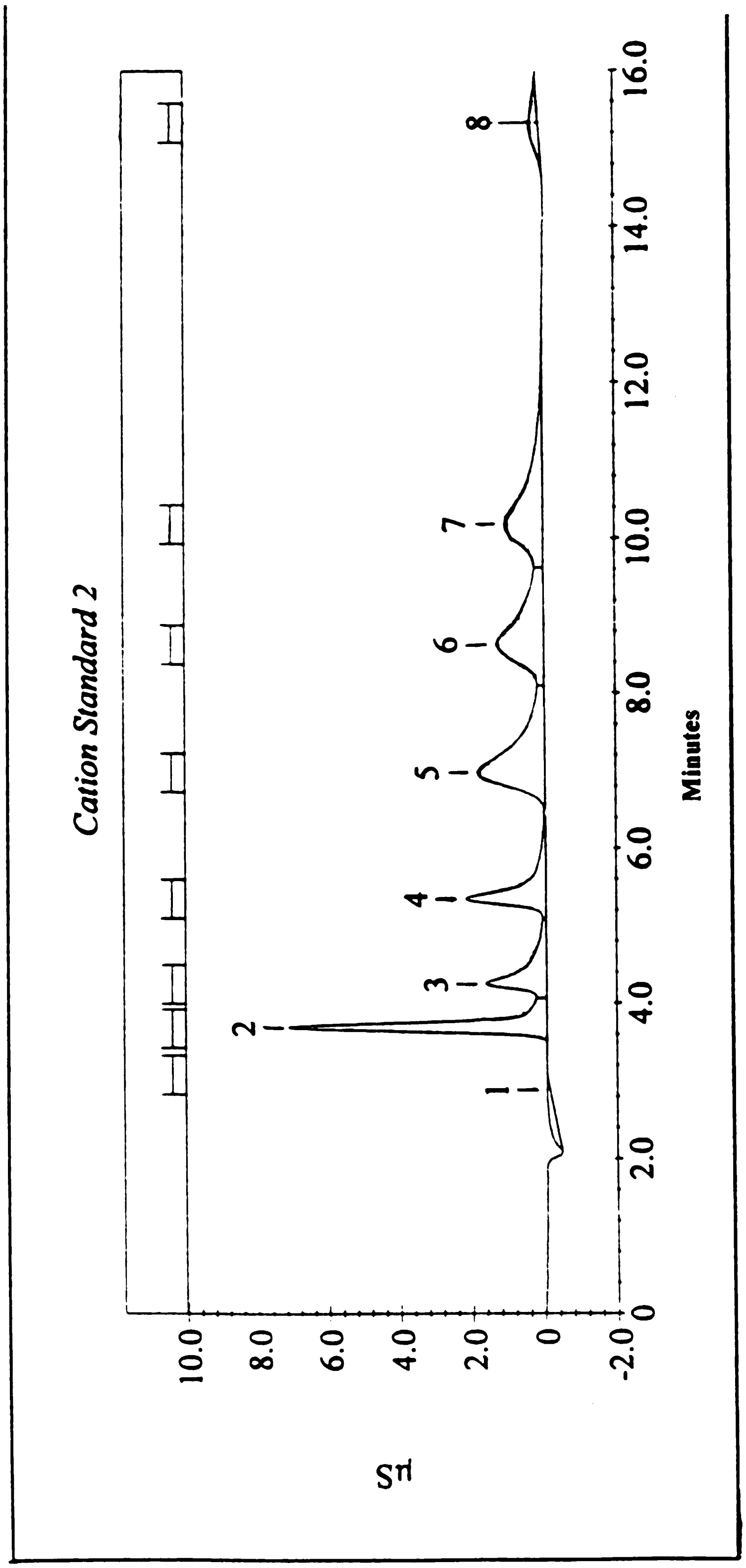
Black Canyon
<22-1560> C6H8O6- Ascorbic Acid <Major>
<05-0377> Niter, syn- KNO3 <Major>
Intensity(counts)
2-Theta(deg)


Black Mag
<71-1558> KNO3- Potassium Nitrate <Major>
<22-1560> C6H8O6- Ascorbic Acid <Major>
<70-0488> KCLO4- Potassium Chlorate <Major>
Intensity(counts)
2-Theta(deg)


Clean Shot
<74-2055> KNO3- Potassium Nitrate <Major>
<07-0211> KClO4- Potassium Chlorate <Major>
<22-1560> C6H8O6- Ascorbic Acid <Major>
Intensity(counts)
2-Theta(deg)

APPENDIX IV

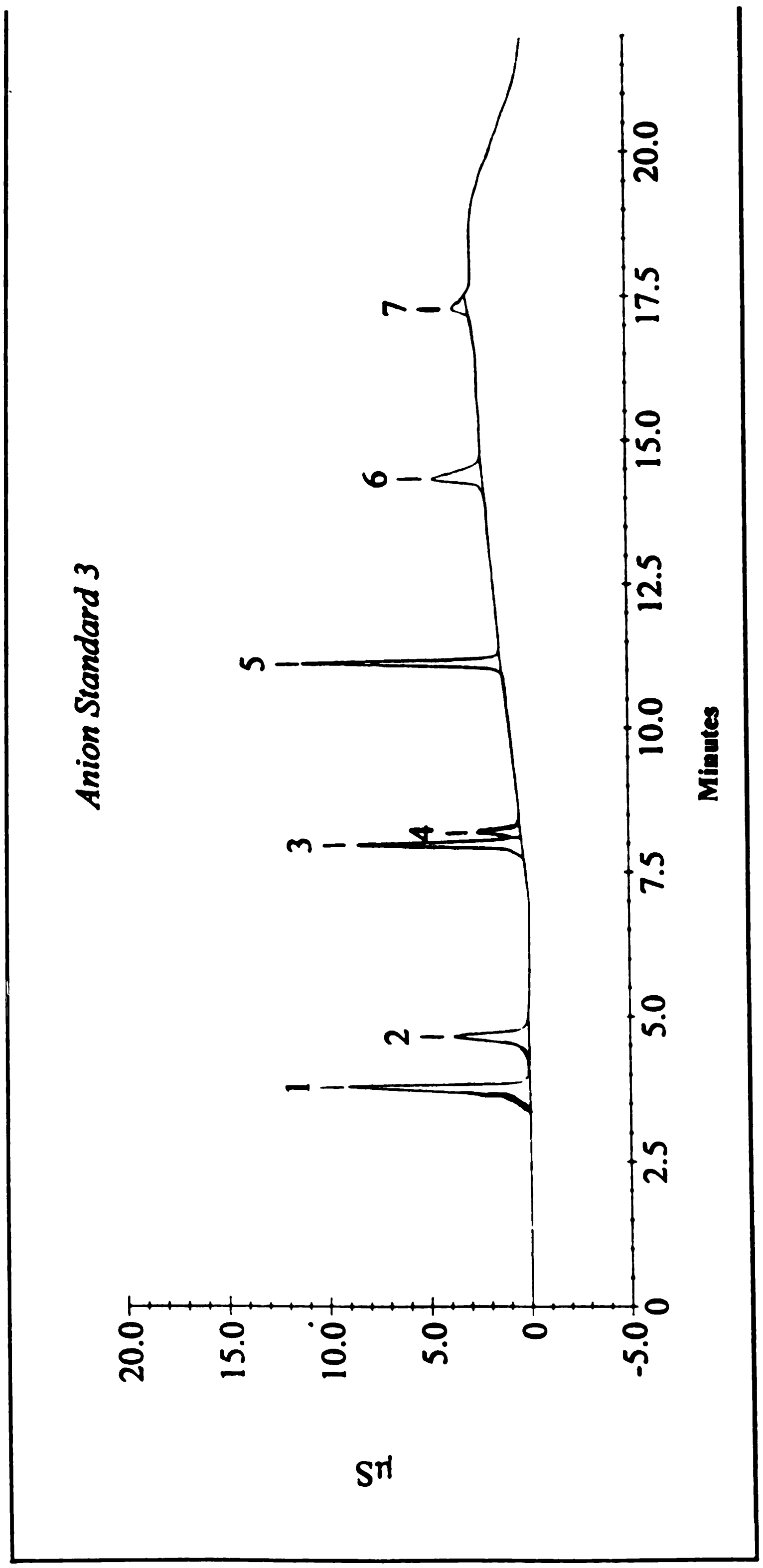
IC Results


Cation Standard 2
µS
10.0
8.0
6.0
4.0
2.0
0
-2.0
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
Minutes
1
2
3
4
5
6
7
8

SAMPLE ANALYSIS REPORT

Sample Name: Cation Standard for Extracts

Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1		2.88	0.00	76562	844
2	Na	3.68	0.00	634865	70663
3	NH_4	4.25	0.00	315169	16613
4	K	5.35	0.00	372645	22008
5	Mg	6.98	0.00	724728	18651
6	Ca	8.63	0.00	604574	13113
7	Sr	10.18	0.00	599446	10676
8	Ba	15.33	0.00	102042	2333

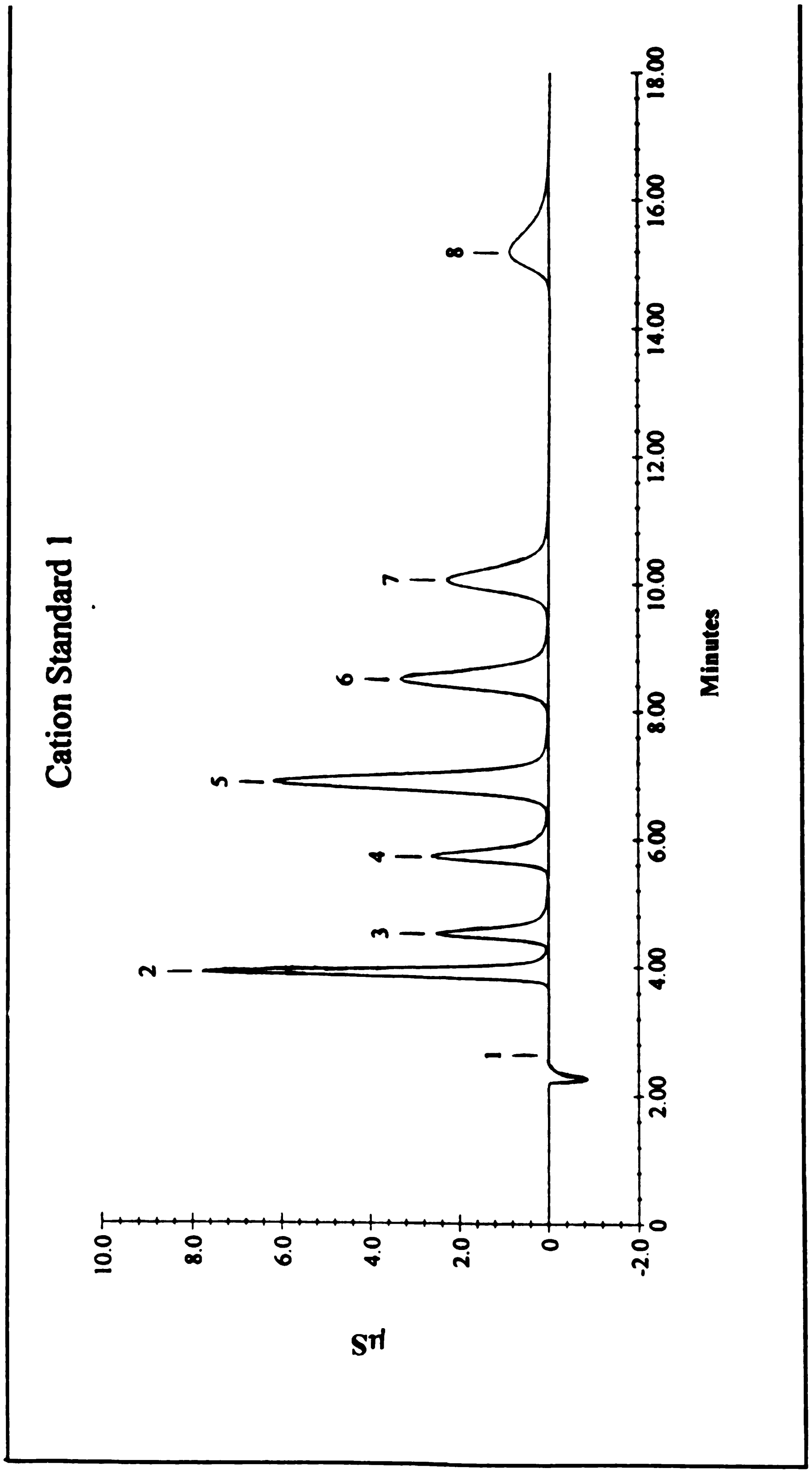


Anion Standard 3
µS
20.0
15.0
10.0
5.0
0
-5.0
0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
Minutes
1
2
3
4
5
6
7

SAMPLE ANALYSIS REPORT

Sample Name: Anion Standard for Extracts

Peak #	Component Name	Retention Time	Amount (ppm)	Peak Area	Peak Height
1	Cl	3.77	0.00	799257	87504
2	NO_2	4.65	9.61	414703	37527
3	NO_3	7.97	0.00	499891	82661
4	ClO_3	8.18	3.31	129776	21196
5	SO_4	11.10	2.55	547312	95330
6	SCN	14.32	8.64	337864	25353
7	ClO_4	17.27	9.54	87879	7795

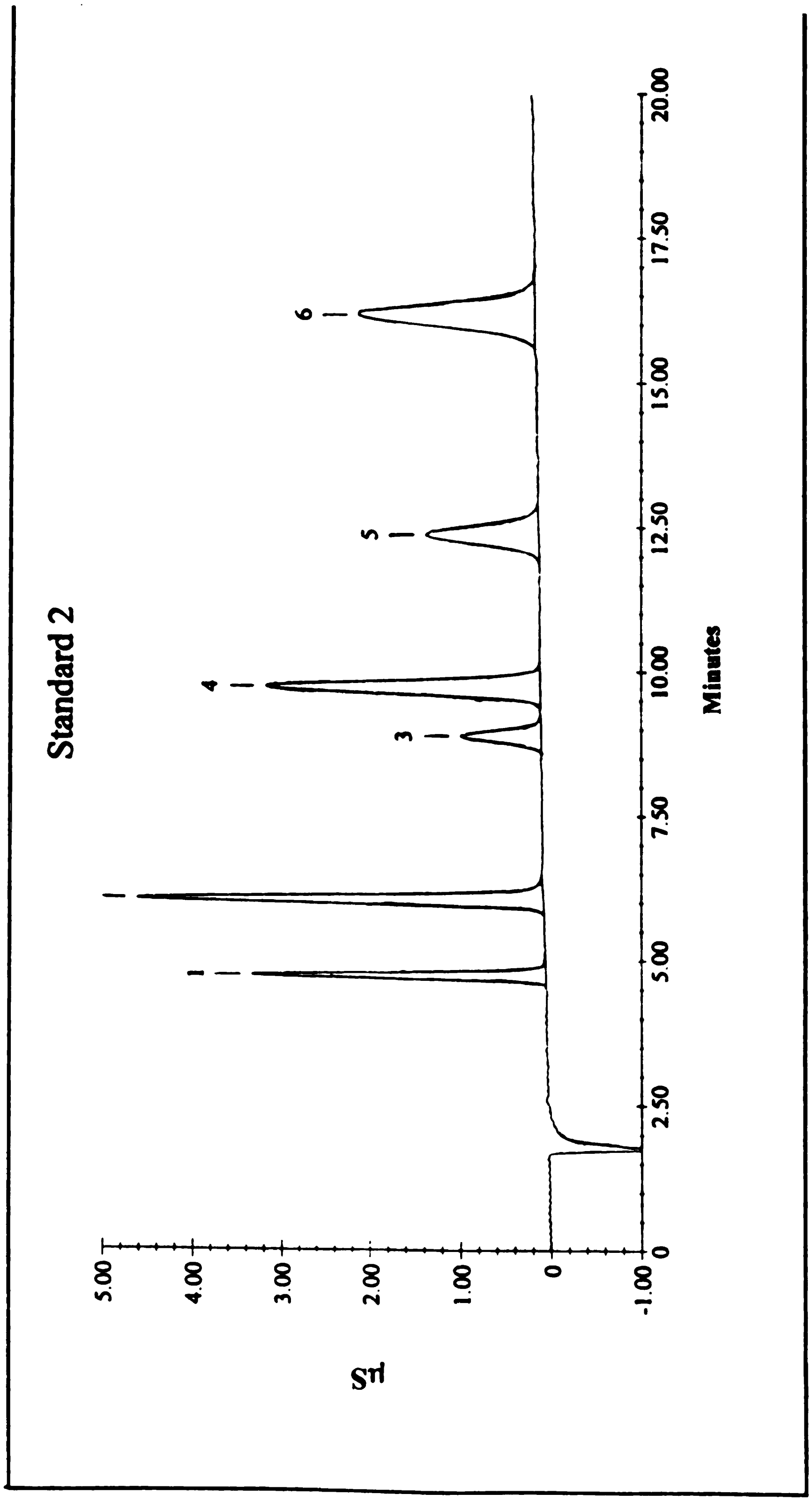


Cation Standard 1
μS
10.0
8.0
6.0
4.0
2.0
0
-2.0
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
Minutes
1
2
3
4
5
6
7
8

SAMPLE ANALYSIS REPORT

Sample Name: Cation Standard for Residues

Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		2.63	583	52	11.16
2	Na	3.90	669028	77654	8.62
3	NH_4	4.52	313656	25429	12.33
4	K	5.72	390974	26086	14.99
5	Mg	6.87	1115834	61582	18.12
6	Ca	8.48	734476	33288	22.06
7	Sr	10.05	623817	23035	27.08
8	Ba	15.16	381525	8849	43.12

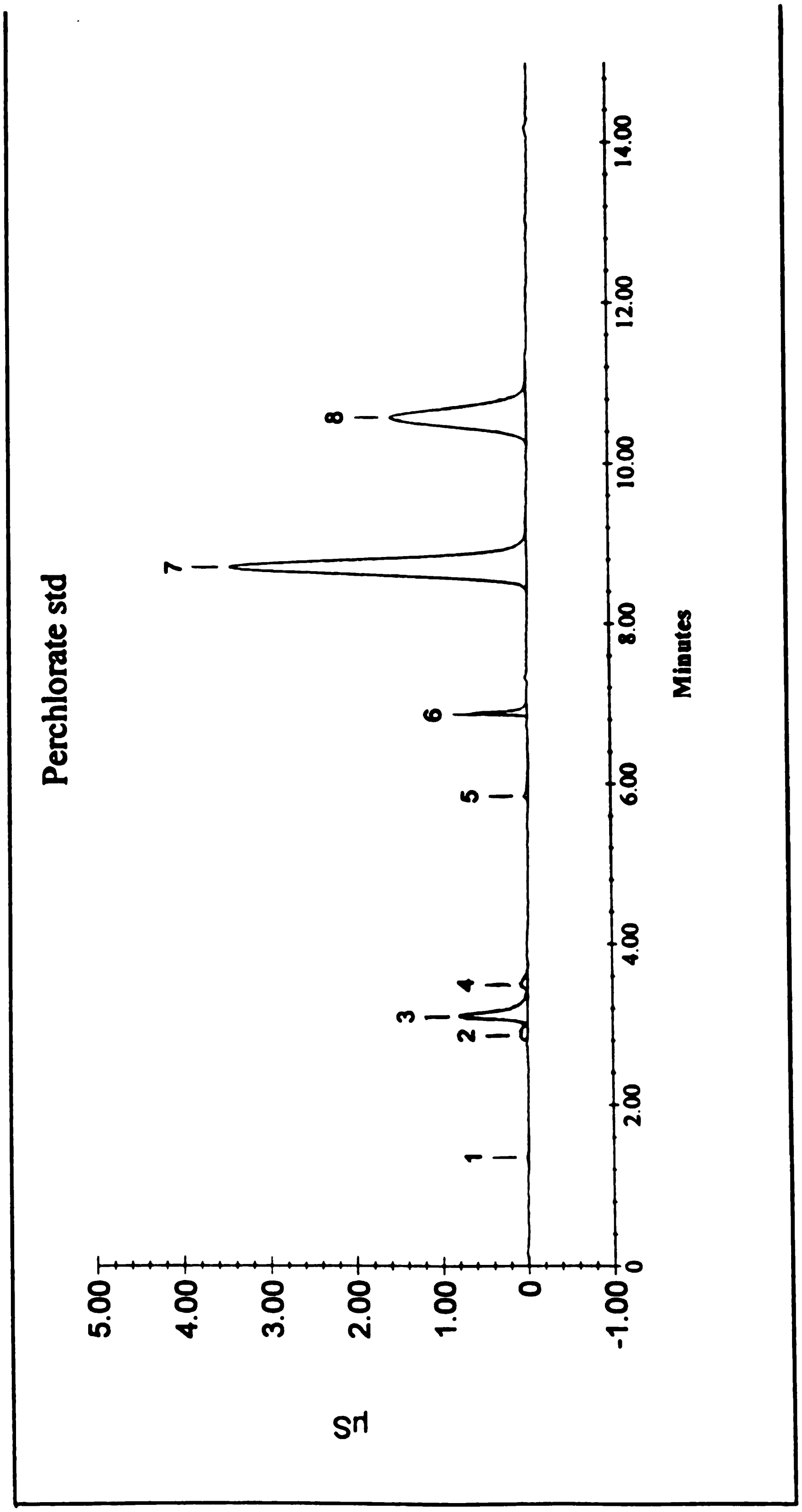


Standard 2
µS
5.00
4.00
3.00
2.00
1.00
0
-1.00
0
2.50
5.00
7.50
10.00
12.50
15.00
17.50
20.00
Minutes
1
3
4
5
6

SAMPLE ANALYSIS REPORT

Sample Name: Anion Standard for Residues

Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1	Cl	4.73	247572	32795	7.55
2	NO_2	6.05	449373	45374	9.90
3	ClO_3	8.88	131277	8946	14.67
4	NO_3	9.72	474116	30648	15.47
5	PO_4	12.37	288817	12485	23.13
6	SO_4	16.15	550364	19563	28.13


Perchlorate std
µS
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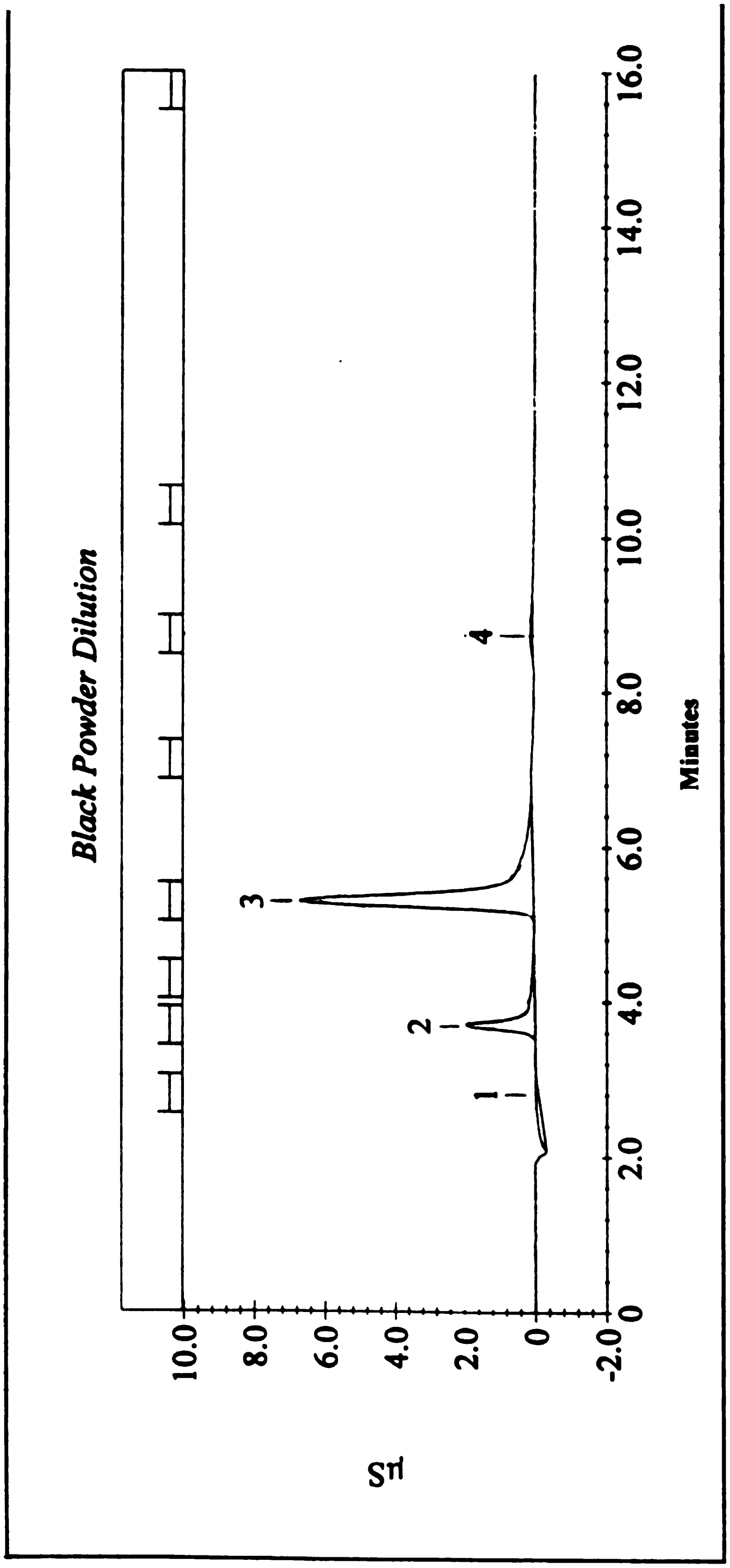
4.00
3.00
2.00
1.00
0
-1.00
1
2
3
4
5
6
7
8
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
Minutes

PERCHLORATE/THIOCYANATE REPORT

Sample Name: Perchlorate Standard

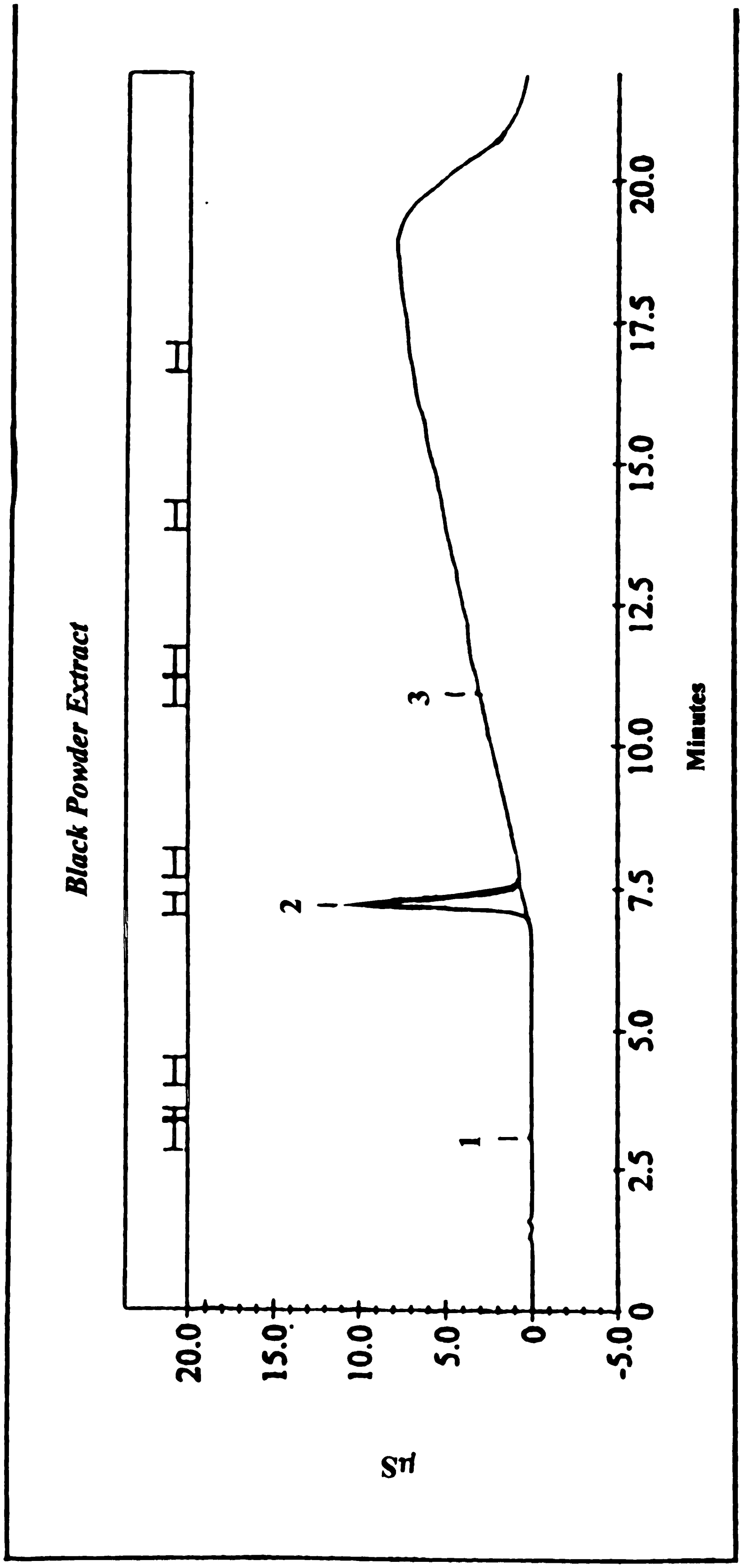
Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		1.35	1813	185	9.77
2		2.87	7121	859	8.29
3		3.10	57502	7964	7.22
4		3.50	6567	952	6.90
5		5.85	4753	547	8.69
6		6.87	19221	4786	4.02
7	SCN	8.70	472264	34837	13.56
8	ClO_4	10.57	265523	16104	16.49


Black Powder Dilution
μS
10.0
8.0
6.0
4.0
2.0
0
-2.0
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
Minutes
1
2
3
4

CATION ANALYSIS REPORT OF EXTRACT

Sample Name: Black Powder Extract

Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1		2.80	0.00	53881	851
2	Na	3.68	0.00	205175	18998
3	K	5.28	0.00	960008	66172
4	Ca	8.73	0.00	17533	678

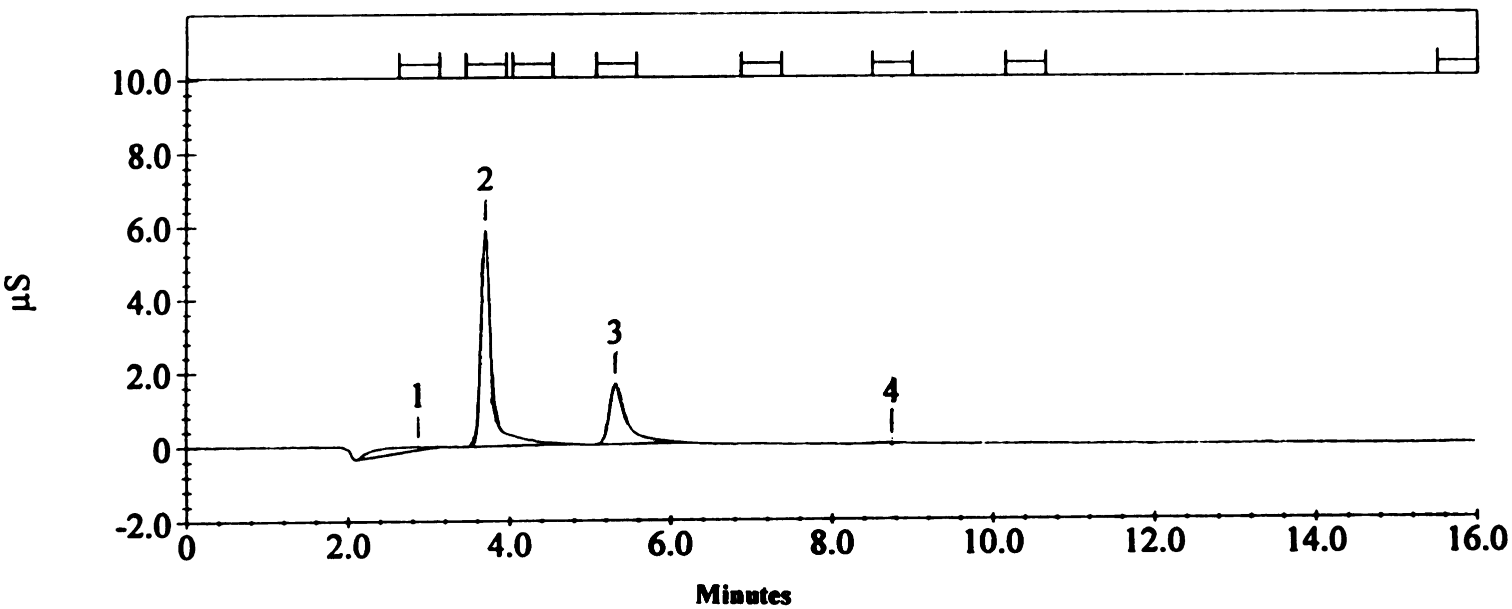

Black Powder Extract
μS
20.0
15.0
10.0
5.0
0
-5.0
0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
Minutes
1
2
3

ANION ANALYSIS REPORT OF EXTRACT

Sample Name: Black Powder Extract

Peak #	Component Name	Retention Time	Amount (ppm)	Peak Area	Peak Height
1		3.07	0.09	14444	2385
2	NO_3	7.20	0.00	1241461	102771
3	SO_4	10.93	0.07	15147	2152

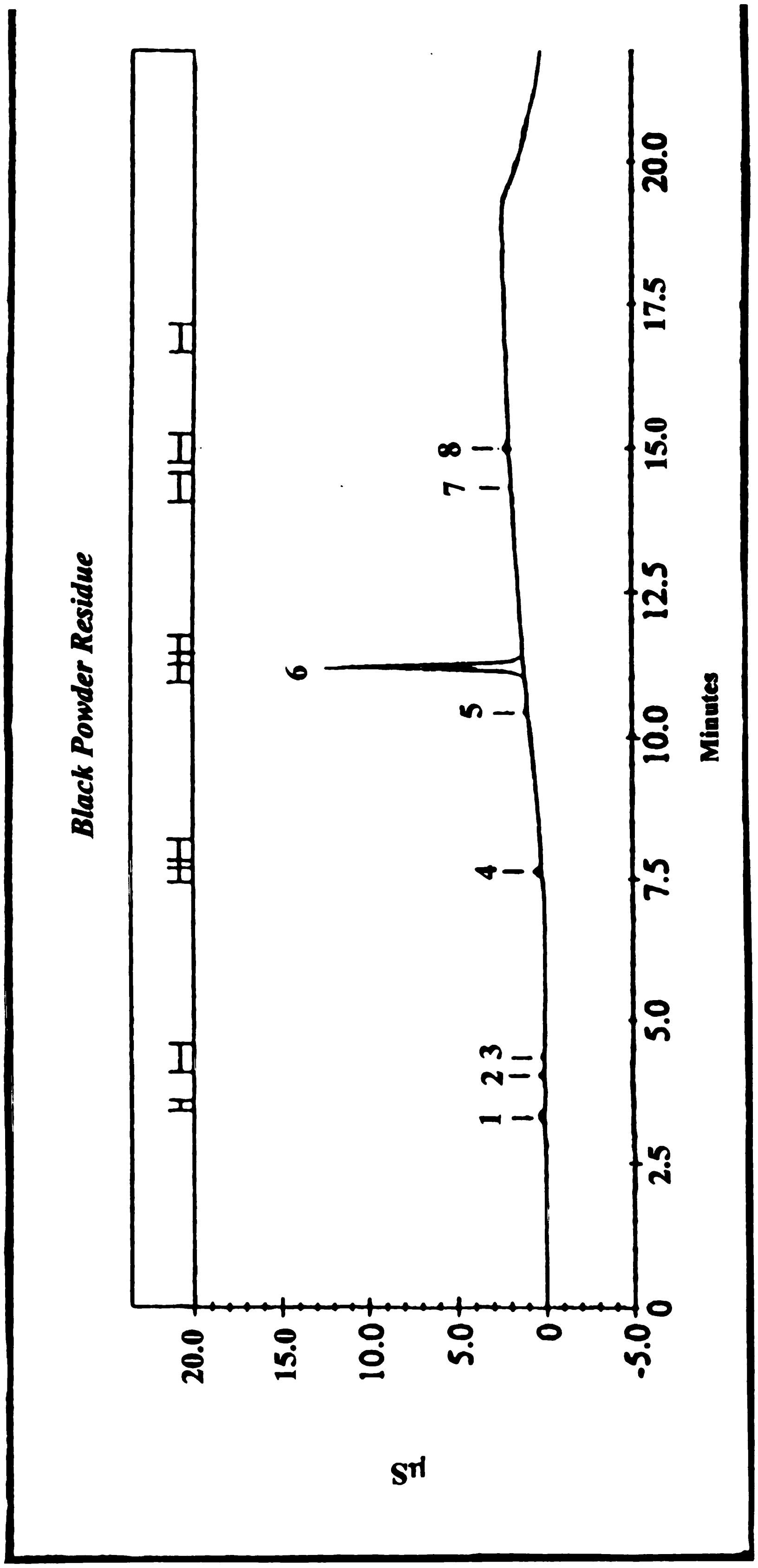
Black Powder Residue



CATION ANALYSIS REPORT OF EXTRACT

Sample Name: Black Powder Residue

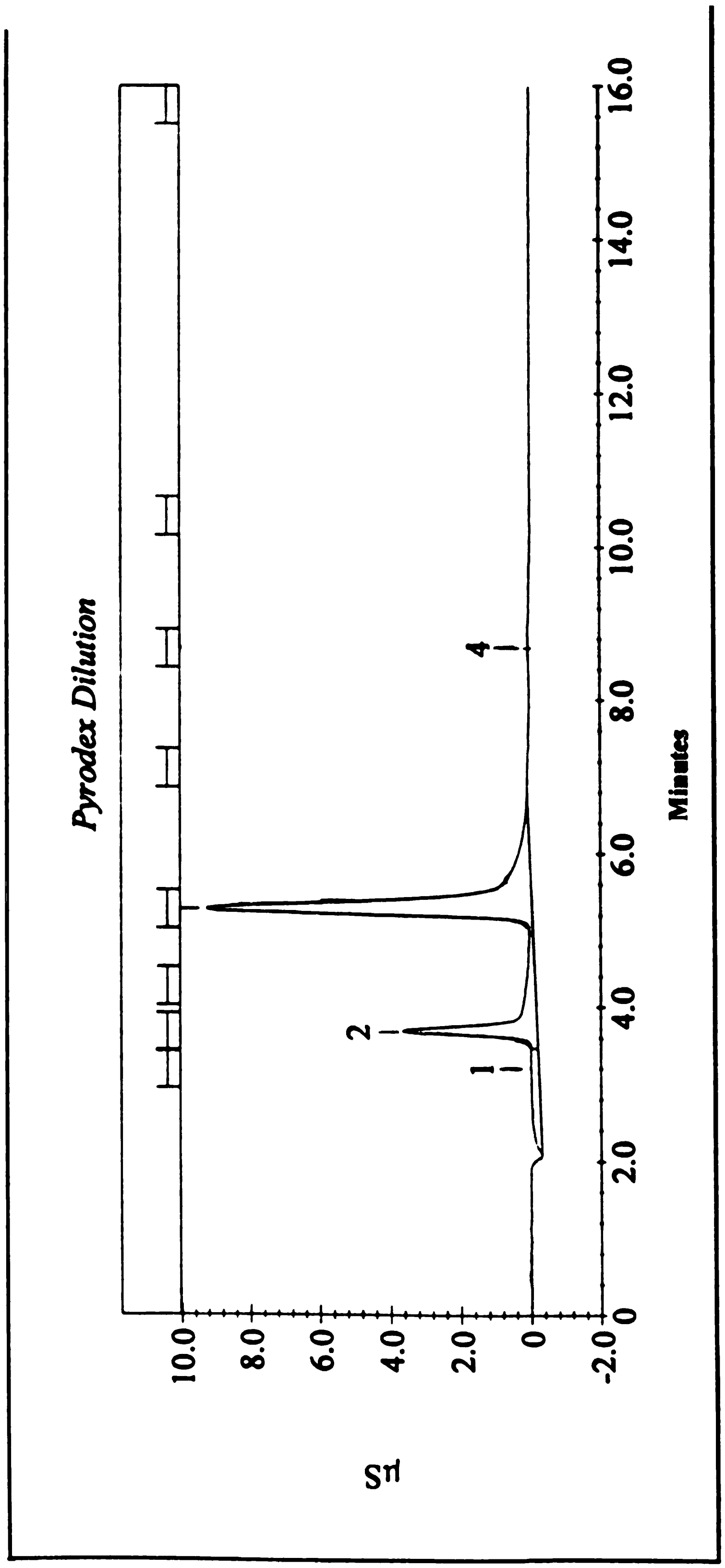
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1		2.87	0.00	71091	896
2	Na	3.70	0.00	555840	58733
3	K	5.32	0.00	250211	16408
4	Ca	8.75	0.00	3229	169


Black Powder Residue
µS
20.0
15.0
10.0
5.0
0
-5.0
0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
Minutes
1
2
3
4
5
6
7
8

ANION ANALYSIS REPORT OF RESIDUE

Sample Name: Black Powder Residue

Peak #	Component Name	Retention Time	Amount (ppm)	Peak Area	Peak Height
1		3.28	0.00	10182	1828
2	NO_2	4.02	0.59	25291	3407
3		4.33	0.00	14461	1881
4	NO_3	7.62	0.00	31484	4854
5		10.38	0.00	2649	2421
6	SO_4	11.17	2.94	631081	96104
7	SCN	14.28	0.26	9971	1165
8		14.97	0.24	40660	3428

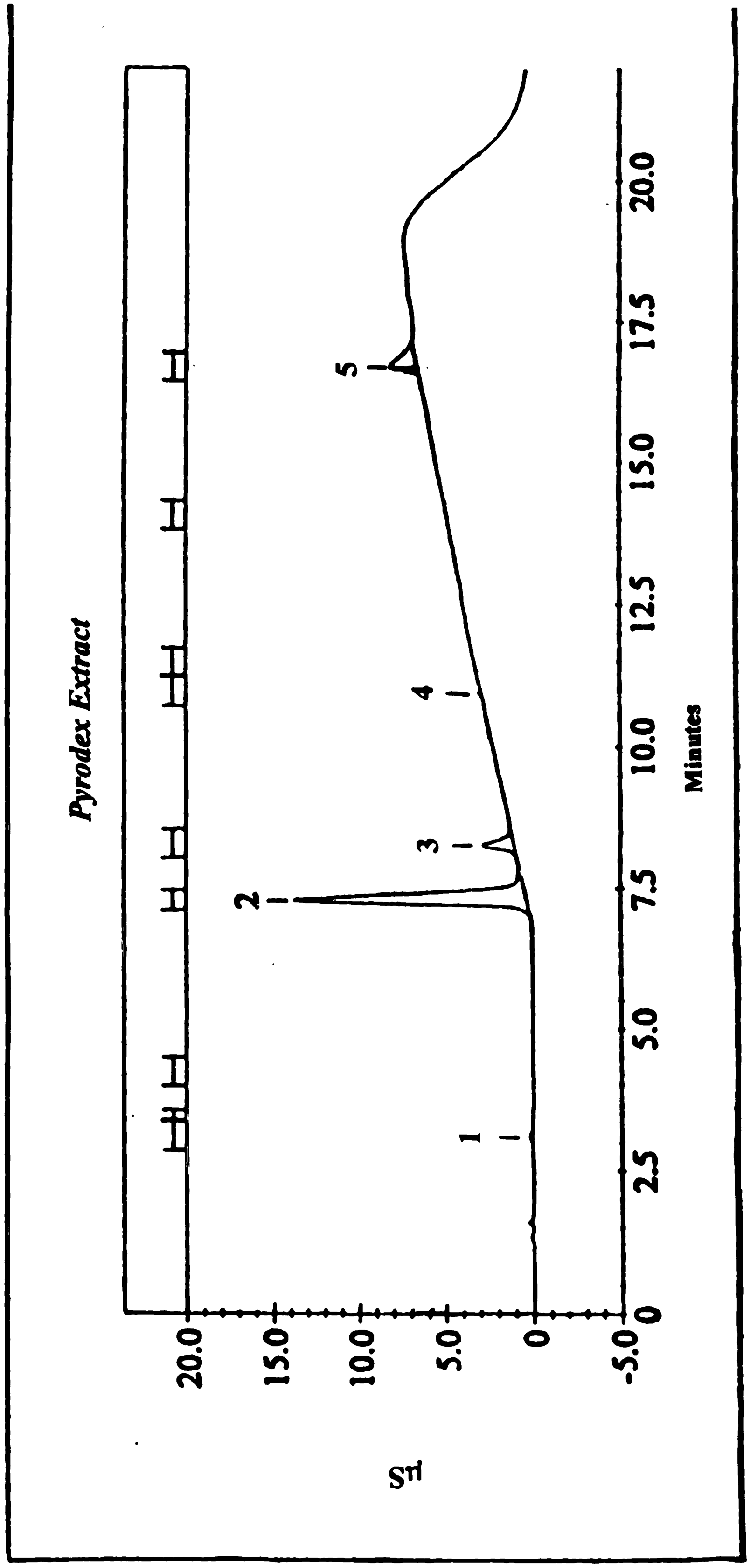


Pyrodex Dilution
µS
10.0
8.0
6.0
4.0
2.0
0
-2.0
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
Minutes
1
2
4

CATION ANALYSIS REPORT OF EXTRACT

Sample Name: Pyrodex Extract

Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1		3.20	0.00	169339	2234
2	Na	3.68	0.00	499108	36866
3	K	5.28	0.00	1357698	92478
4	Ca	8.68	0.00	1687	175

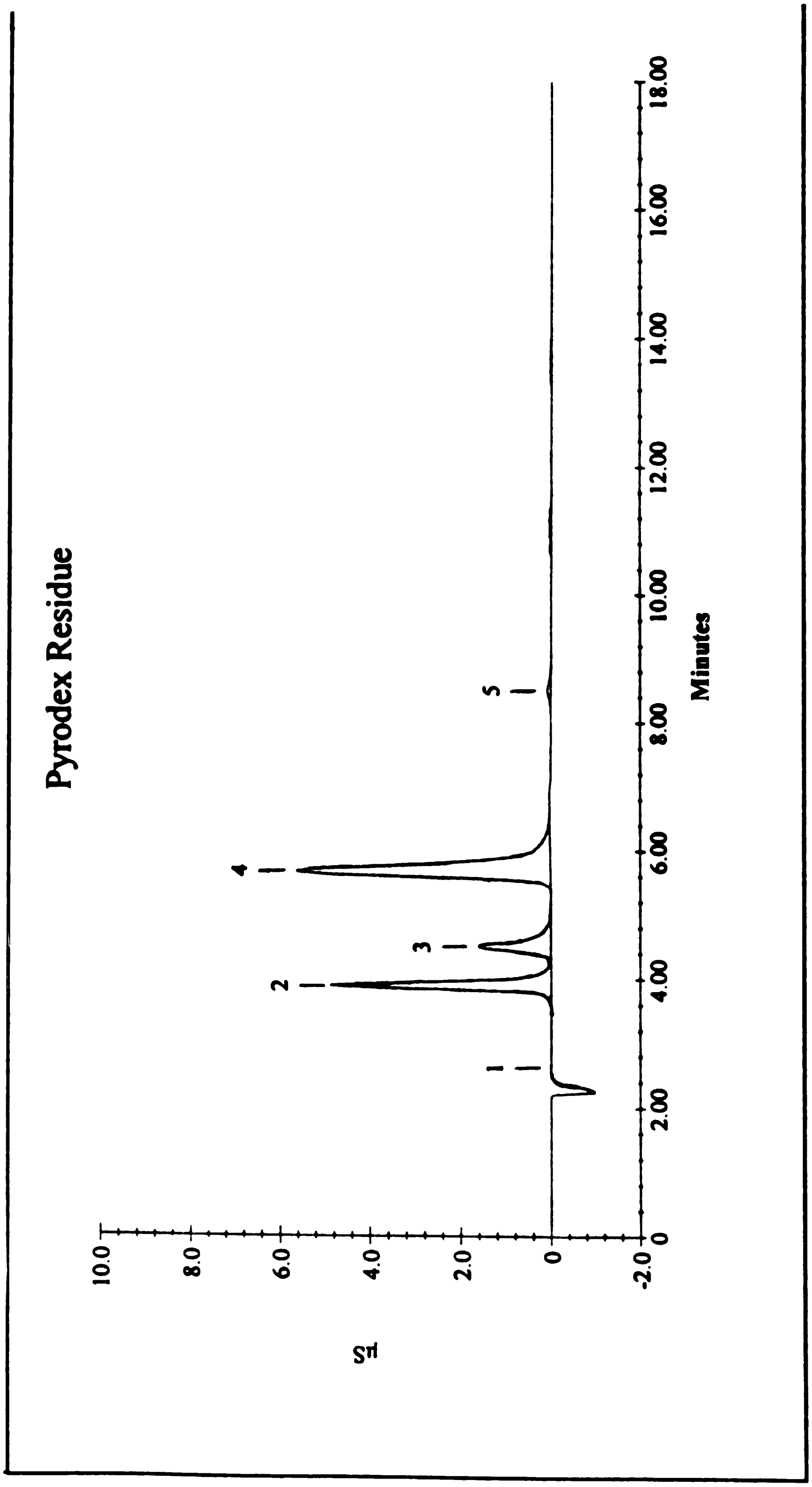


Pyrodex Extract
μS
20.0
15.0
10.0
5.0
0
-5.0
0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
Minutes
1
2
3
4
5

ANION ANALYSIS REPORT OF EXTRACT

Sample Name: Pyrodex Extract

Peak #	Component Name	Retention Time	Amount (ppm)	Peak Area	Peak Height
1		3.10	0.07	11175	1894
2	NO_3	7.27	0.00	1629629	132734
3	ClO_3	8.27	4.89	191845	18296
4	SO_4	10.95	0.22	46307	1584
5	ClO_4	16.68	30.65	282433	15504

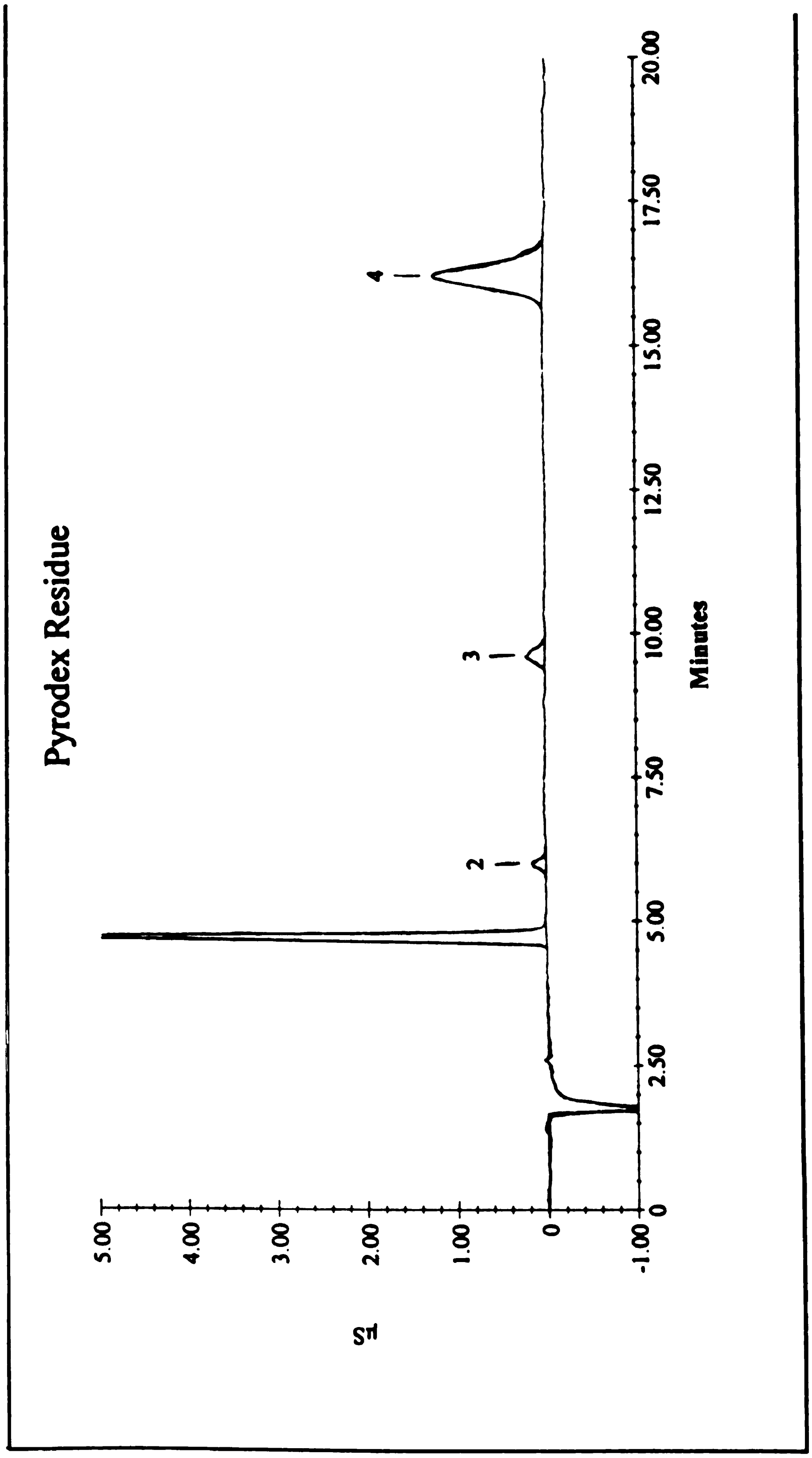


Pyrodex Residue
µS
10.0
8.0
6.0
4.0
2.0
0
-2.0
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
Minutes
1
2
3
4
5

CATION ANALYSIS REPORT OF RESIDUE

Sample Name: Pyrodex Residue

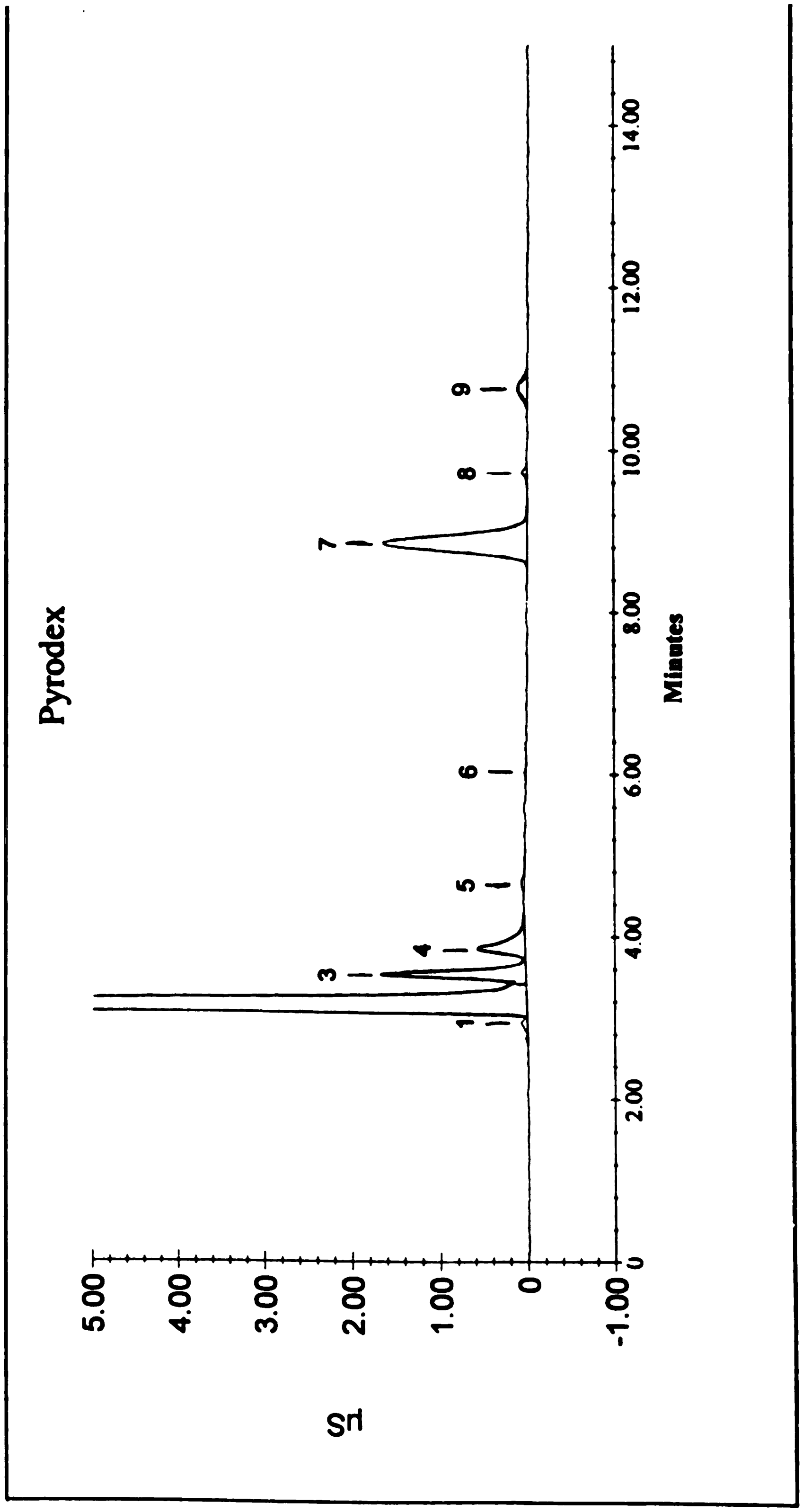
Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		2.62	1382	83	16.69
2	Na	3.88	416629	47608	8.75
3	NH_4	4.50	187528	16095	11.65
4	K	5.67	811753	56461	14.38
5	Ca	8.50	15241	751	20.28


Pyrodex Residue
µS
5.00
4.00
3.00
2.00
1.00
0
-1.00
2
3
4
0
2.50
5.00
7.50
10.00
12.50
15.00
17.50
20.00
Minutes

ANION ANALYSIS REPORT OF RESIDUE

Sample Name: Pyrodex Residue

Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1	Cl	4.70	436808	58188	7.51
2	NO_2	6.00	18581	1615	11.51
3	NO_3	9.62	430144	1968	15.32
4	SO_4	16.20	344236	12418	27.72

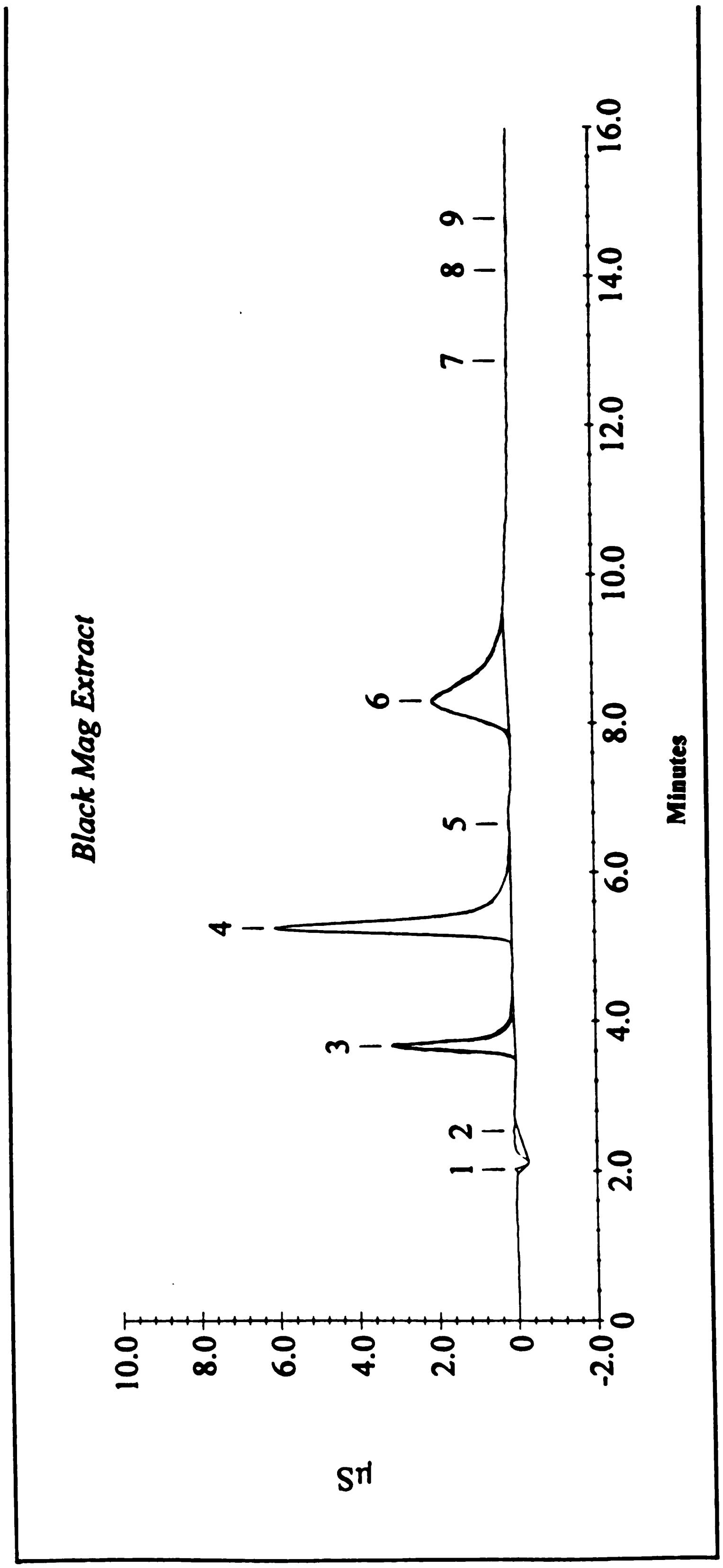


Pyrodex
µS
5.00
4.00
3.00
2.00
1.00
0
-1.00
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
Minutes
1
3
4
5
6
7
8
9

PERCHLORATE/THIOCYANATE REPORT

Sample Name: Pyrodex Residue

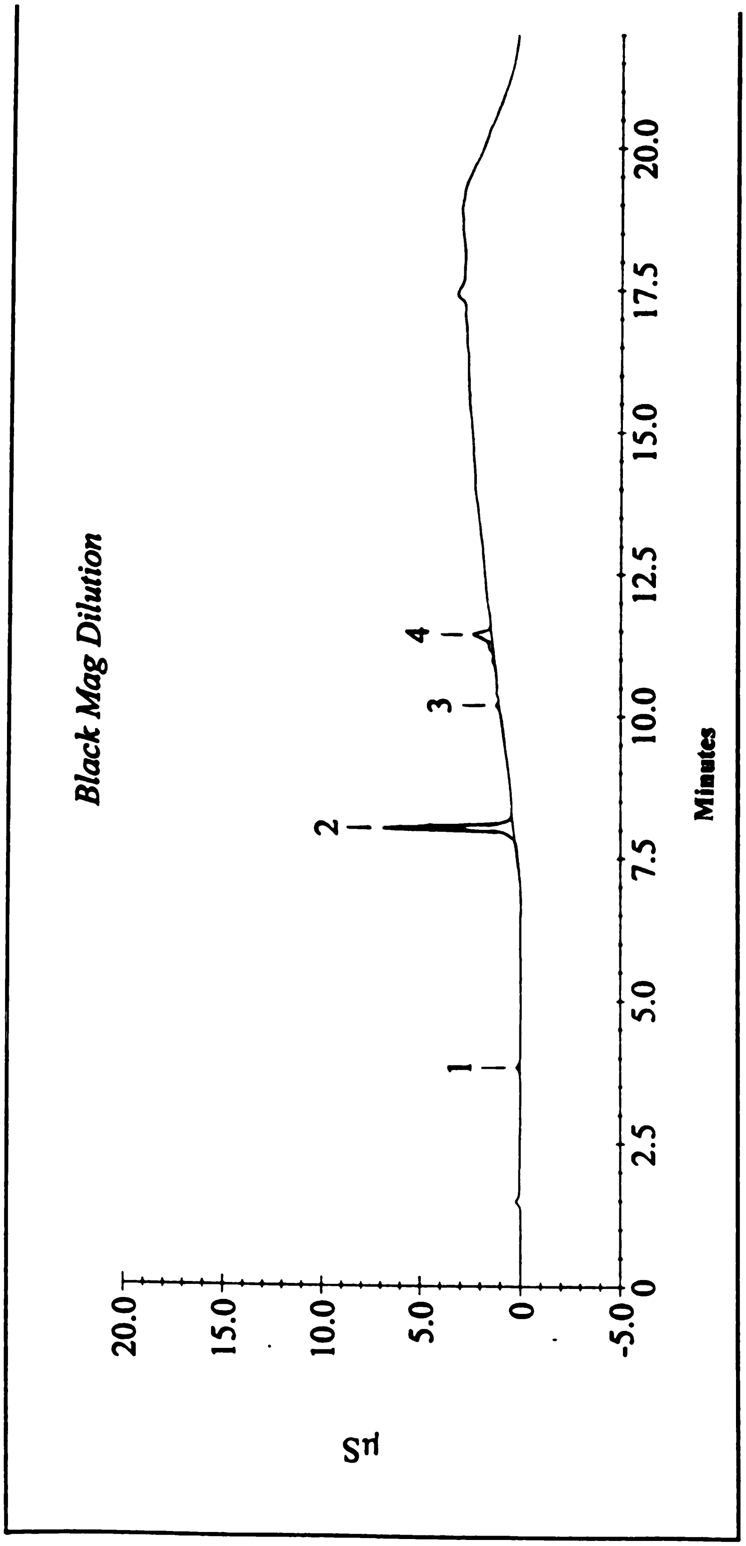
Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		2.93	5718	751	7.61
2		3.15	1449592	179448	8.08
3		3.52	105385	16242	6.49
4		3.83	55384	5373	10.31
5		4.63	3285	340	9.68
6		6.03	1136	251	4.52
7	SCN	8.83	233250	16433	14.19
8		9.72	3162	587	5.38
9	ClO_4	10.75	19739	1214	16.26


Black Mag Extract
µS
10.0
8.0
6.0
4.0
2.0
0
-2.0
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
Minutes
1
2
3
4
5
6
7
8
9

CATION ANALYSIS REPORT OF EXTRACT

Sample Name: Black Mag Extract

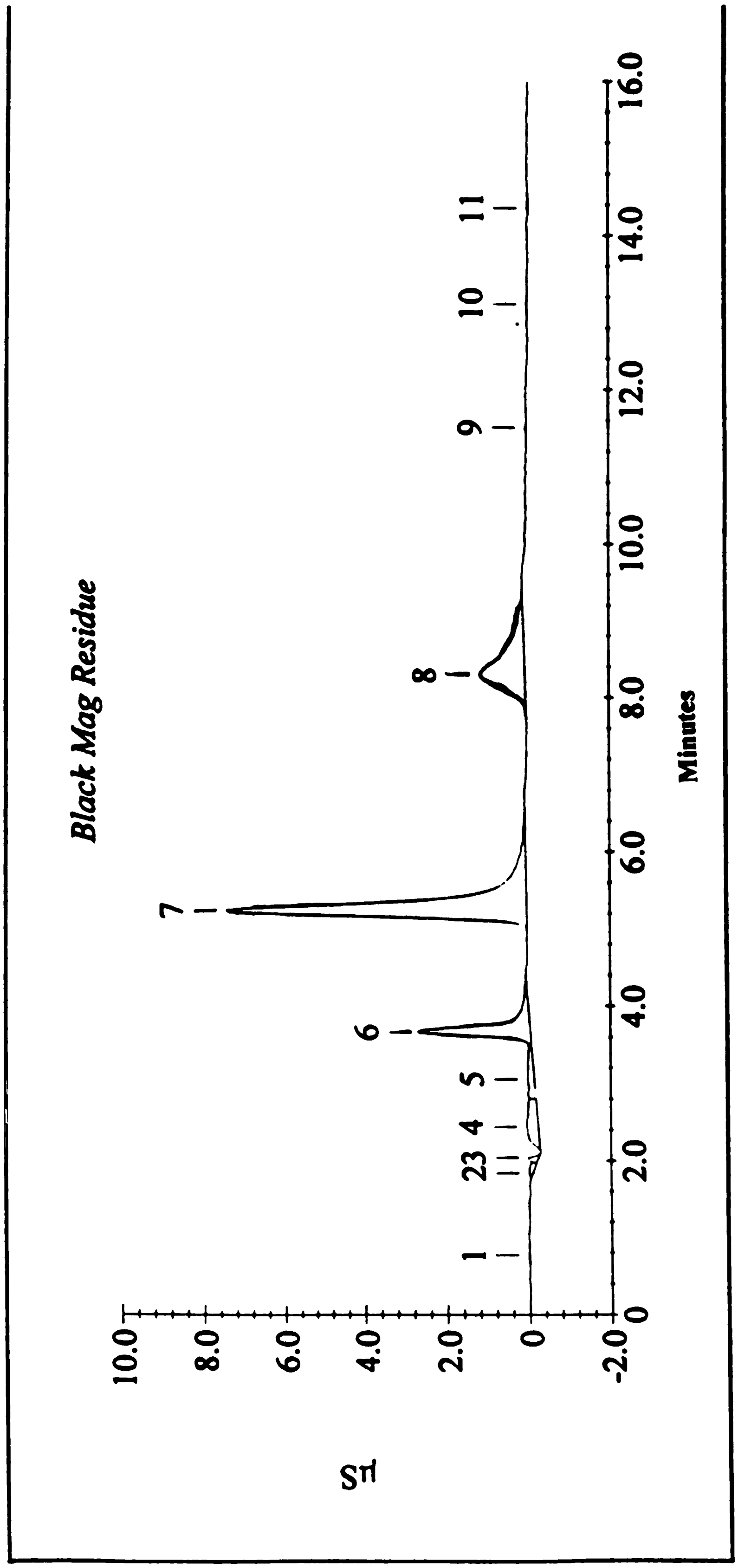
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1		2.02	0.00	6884	1912
2		2.53	0.00	44230	1193
3	Na	3.67	0.00	302911	31345
4	K	5.25	0.00	851674	60035
5	Mg	6.65	0.00	1867	282
6	Ca	8.30	0.00	693786	19318
7		12.85	0.00	1315	231
8		14.07	0.00	1278	191
9		14.77	0.00	1754	206


Black Mag Dilution
µS
20.0
15.0
10.0
5.0
0
-5.0
1
2
3
4
0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
Minutes

ANION ANALYSIS REPORT OF EXTRACT

Sample Name: Black Mag Extract

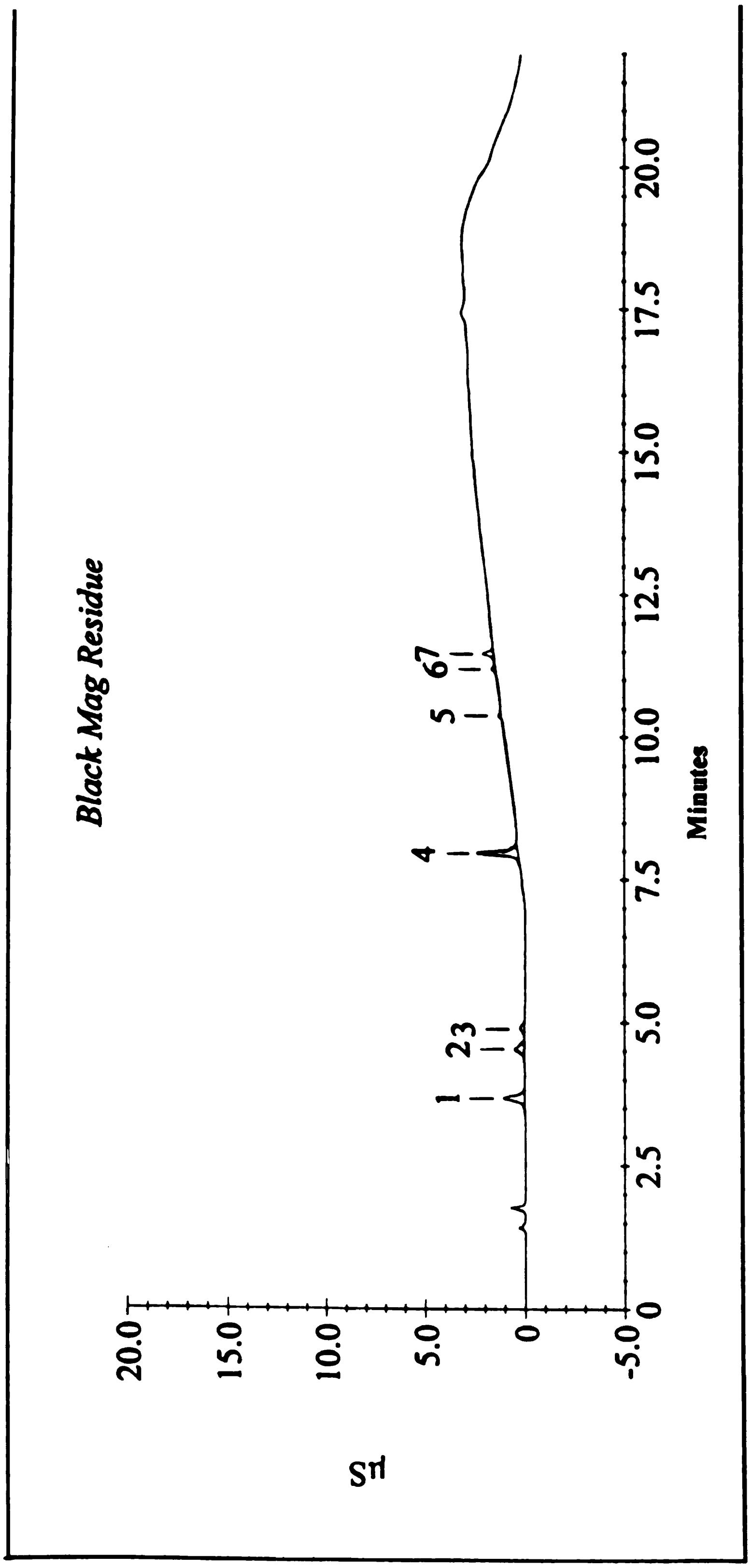
Peak #	Component Name	Retention Time	Amount (ppm)	Peak Area	Peak Height
1	Cl	3.82	0.00	11531	1819
2	NO_3	8.02	9.70	380416	66272
3		10.18	0.00	1606	1590
4	SO_4	11.42	0.48	103217	9057


Black Mag Residue
µS
10.0
8.0
6.0
4.0
2.0
0
-2.0
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
Minutes
1
23
4
5
6
7
8
9
10
11

CATION ANALYSIS REPORT OF EXTRACT

Sample Name: Black Mag Residue

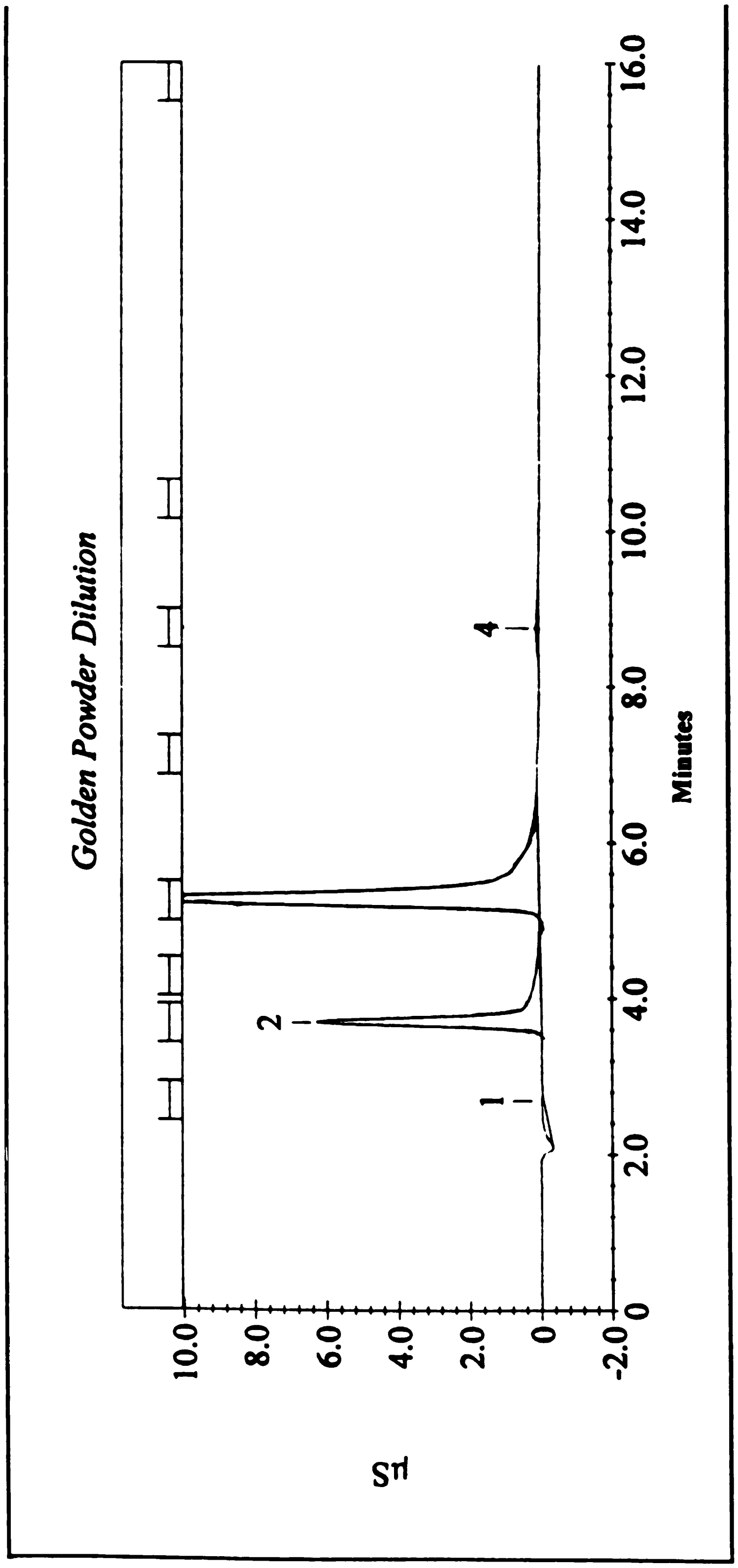
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1		0.77	0.00	1471	177
2		1.83	0.00	12758	908
3		2.03	0.00	9906	2360
4		2.43	0.00	86941	2792
5		3.05	0.00	42214	1603
6	Na	3.65	0.00	280054	26449
7	K	5.22	0.00	1036904	73850
8	Ca	8.28	0.00	376372	11016
9		11.50	0.00	1259	227
10		13.10	0.00	2611	258
11		14.35	0.00	2963	274


Black Mag Residue
µS
20.0
15.0
10.0
5.0
0
-5.0
0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
Minutes
1
2 3
4
5
6 7

ANION ANALYSIS REPORT OF RESIDUE

Sample Name: Black Mag Residue

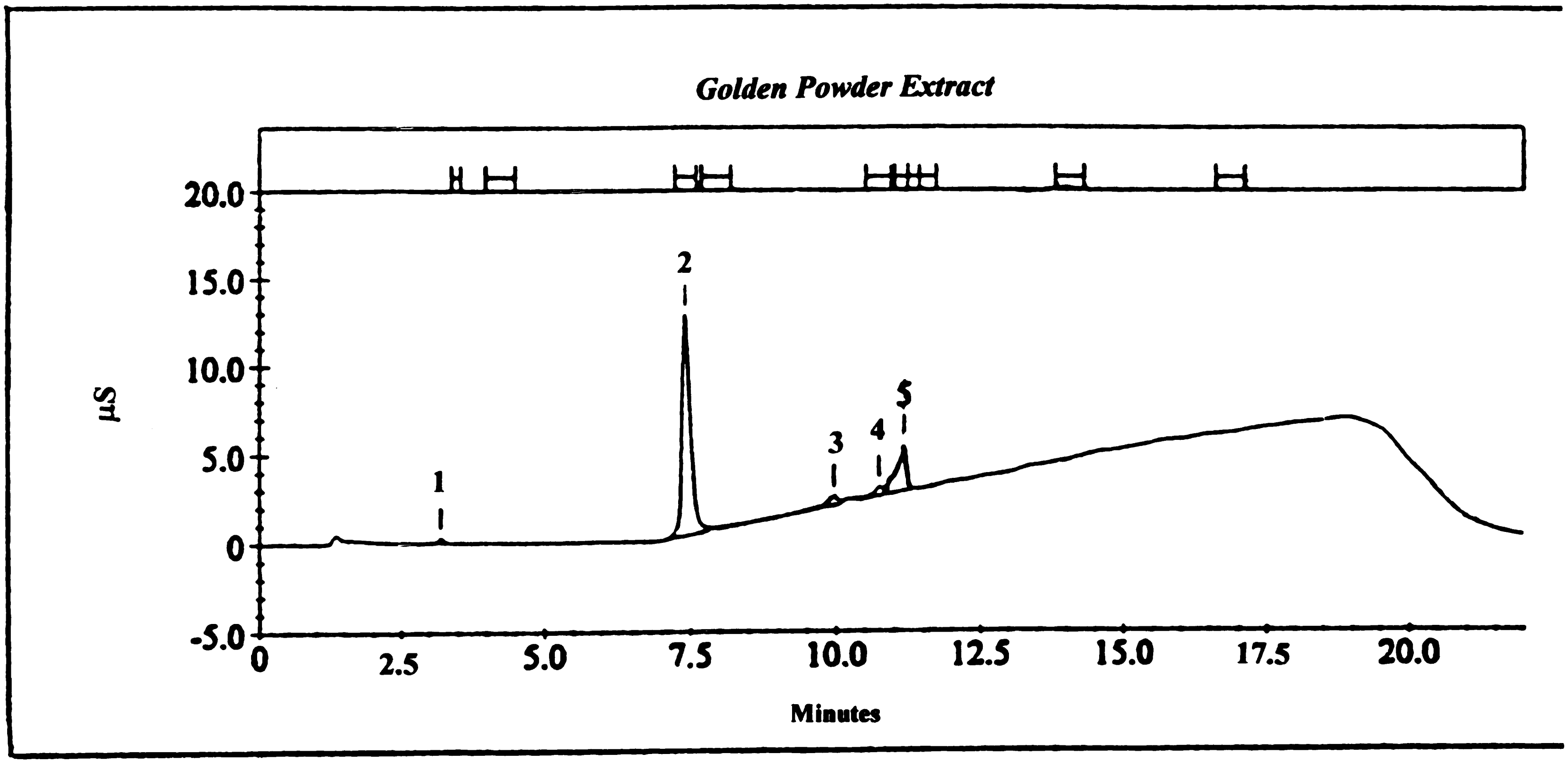
Peak #	Component Name	Retention Time	Amount (ppm)	Peak Area	Peak Height
1	Cl	3.67	0.00	74202	10286
2	NO_2	4.53	0.91	39187	4798
3		4.88	0.00	20934	2310
4	NO_3	7.95	0.00	113201	19286
5		10.37	0.00	31511	1357
6		11.18	0.00	13305	2164
7	SO_4	11.45	0.14	31085	5220


Golden Powder Dilution
µS
10.0
8.0
6.0
4.0
2.0
0
-2.0
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
Minutes
1
2
4

CATION ANALYSIS REPORT OF EXTRACT

Sample Name: Golden Powder Extract

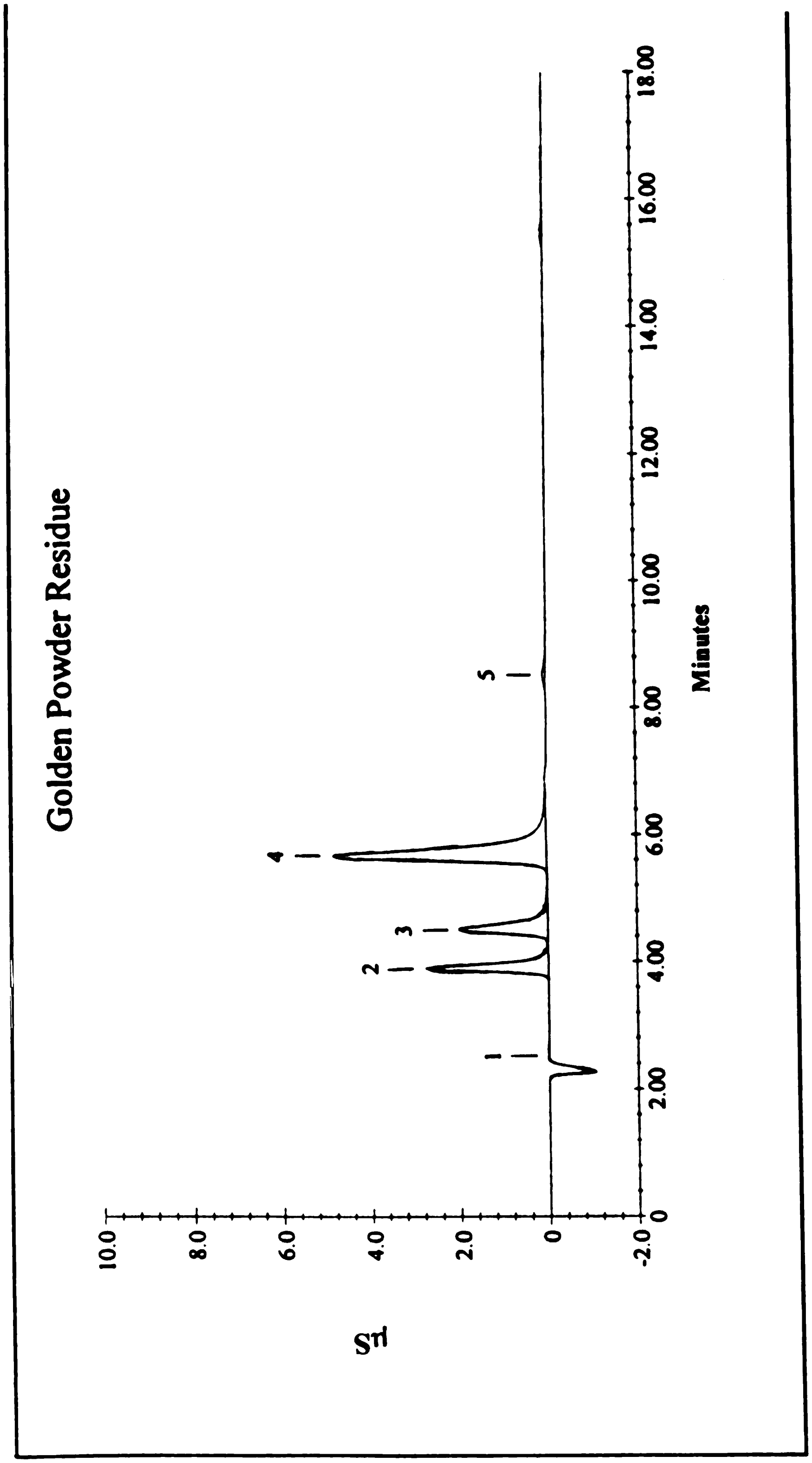
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1		2.68	0.00	39226	560
2	Na	3.68	0.00	603999	61985
3	K	5.25	0.00	1650608	117988
4	Ca	8.75	0.00	23434	734


Golden Powder Extract
20.0
15.0
10.0
5.0
0
-5.0
µS
1
2
3
4
5
0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
Minutes

ANION ANALYSIS OF EXTRACT

Sample Name: Golden Powder Extract

Peak #	Component Name	Retention Time	Amount (ppm)	Peak Area	Peak Height
1		3.20	0.00	18682	2957
2	NO_3	7.40	0.00	1309077	125326
3		9.97	0.00	72683	5358
4	SO_4	10.75	0.30	64786	5511
5		11.18	7.06	331586	25007

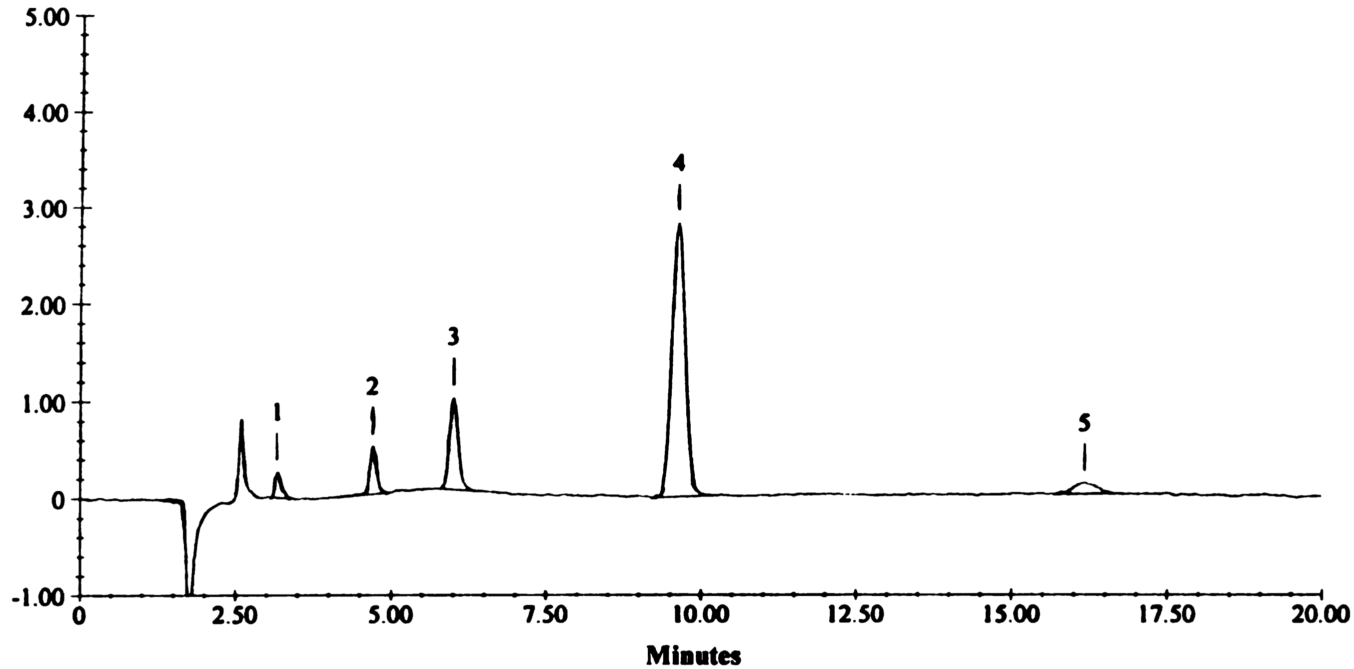

Golden Powder Residue
µS
10.0
8.0
6.0
4.0
2.0
0
-2.0
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
Minutes
1
2
3
4
5

CATION ANALYSIS REPORT OF RESIDUE

Sample Name: Golden Powder Residue

Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		2.51	3627	248	14.63
2	Na	3.90	235142	27789	8.46
3	NH_4	4.50	236907	1999	11.85
4	K	5.67	701437	48673	14.41
5	Ca	8.52	11194	652	17.16

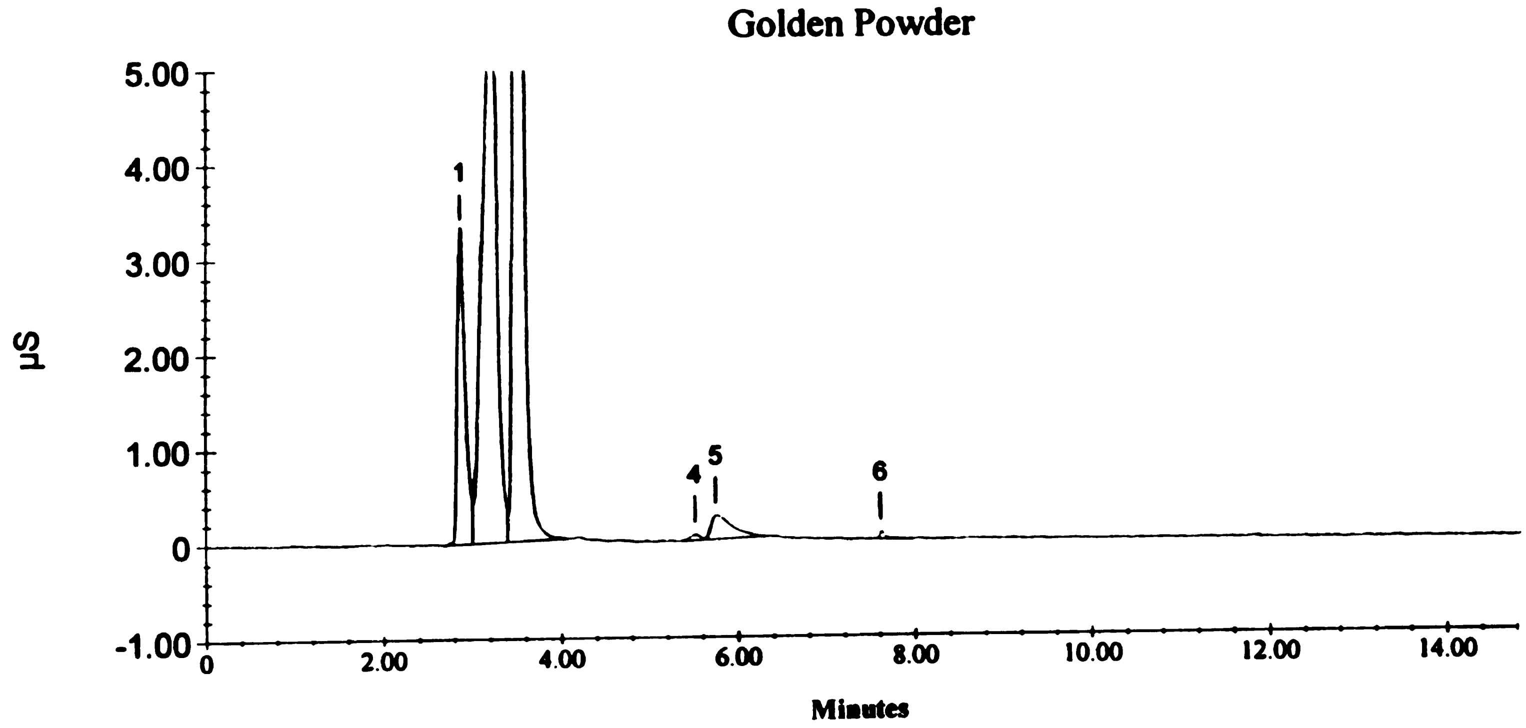
Golden Powder Residue



ANION ANALYSIS REPORT OF RESIDUE

Sample Name: Golden Powder Residue

Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		3.17	17440	2633	6.62
2	Cl	4.70	41957	4904	8.56
3	NO_2	6.00	95115	9521	9.99
4	NO_3	9.62	436596	28321	15.42
5		16.17	29922	1119	26.73

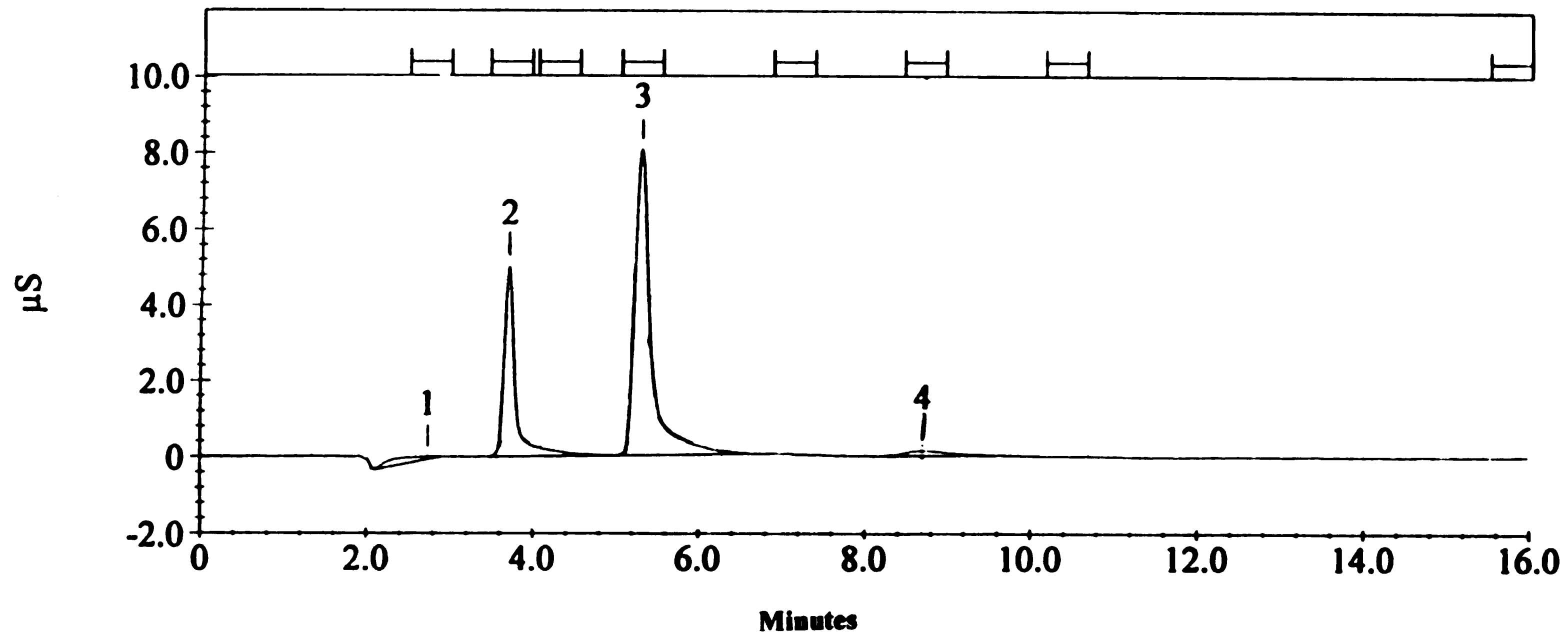

Golden Powder
µS
5.00
4.00
3.00
2.00
1.00
0
-1.00
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
Minutes
1
4
5
6

PERCHLORATE/THIOCYANATE REPORT

Sample Name: Golden Powder Residue

Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		2.87	207295	32897	6.30
2		3.23	657067	57088	11.51
3		3.52	1146162	184473	6.21
4		5.52	5391	633	8.52
5		5.75	41878	2501	16.75
6		7.62	4359	790	5.52

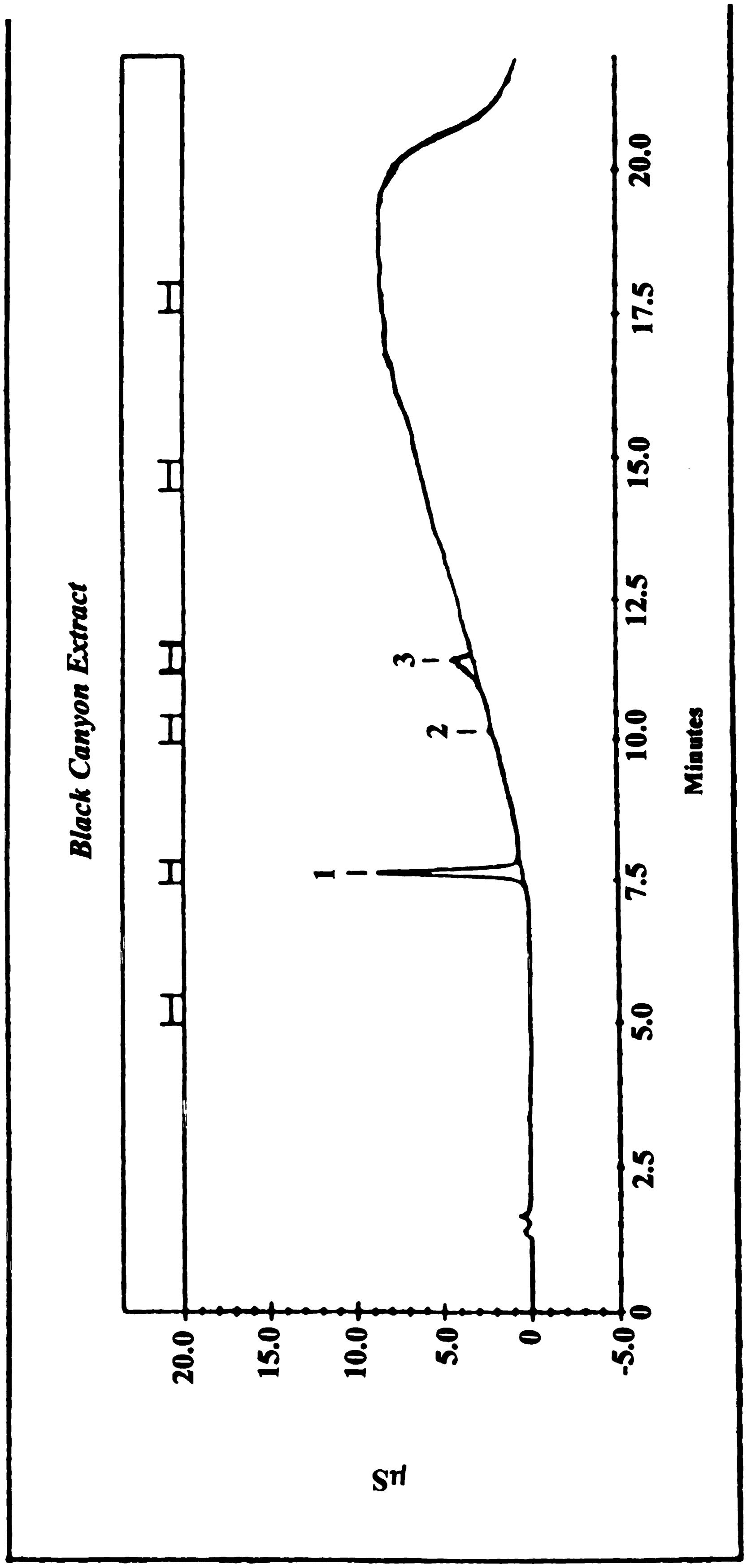
Black Canyon Dilution



CATION ANALYSIS REPORT OF EXTRACT

Sample Name: Black Canyon Extract

Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1		2.73	0.00	49960	782
2	Na	3.70	0.00	491495	50325
3	K	5.28	0.00	1139858	80472
4	Ca	8.70	0.00	53130	1433

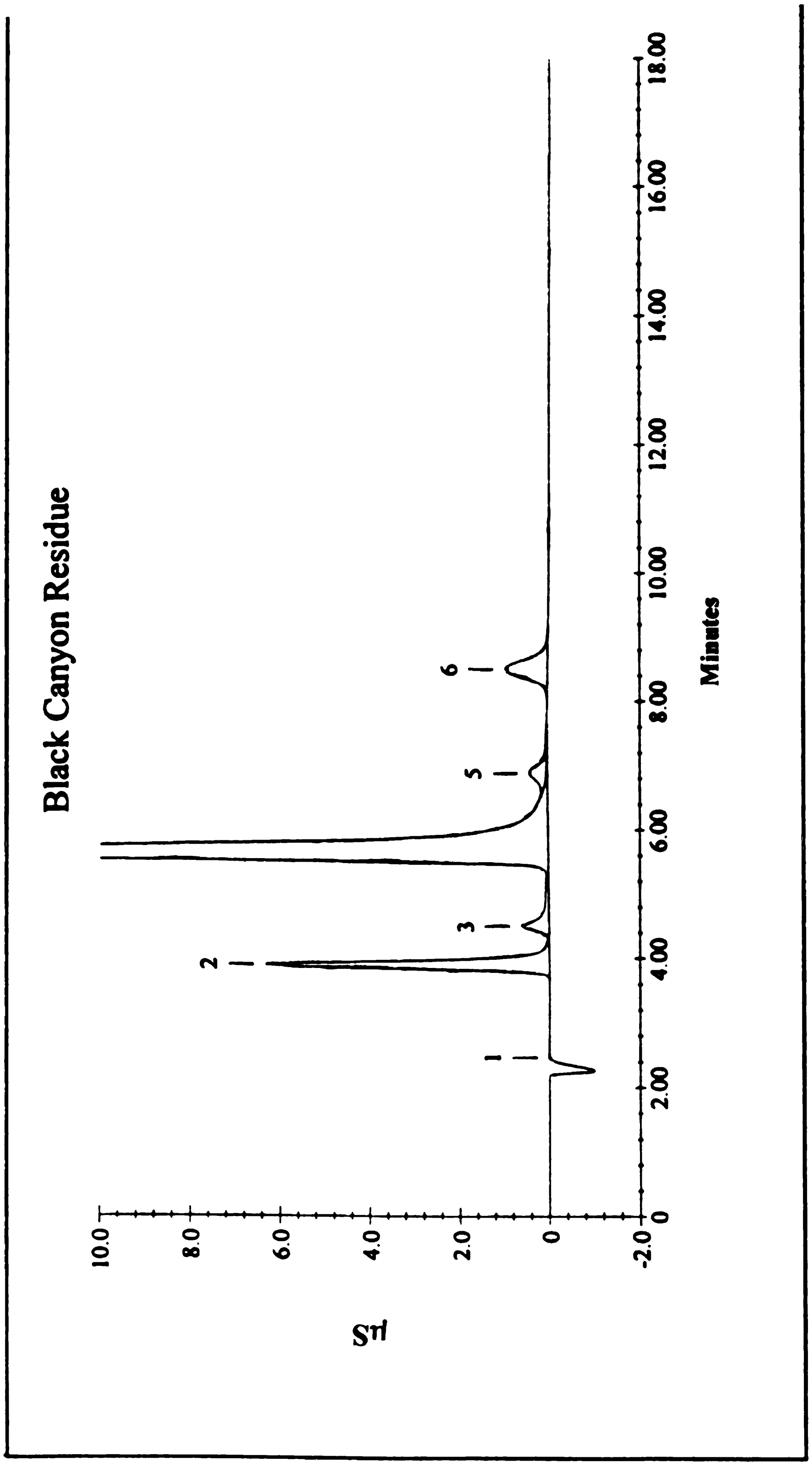


Black Canyon Extract
µS
20.0
15.0
10.0
5.0
0
-5.0
1
2
3
0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
Minutes

ANION ANALYSIS REPORT OF EXTRACT

Sample Name: Black Canyon Extract

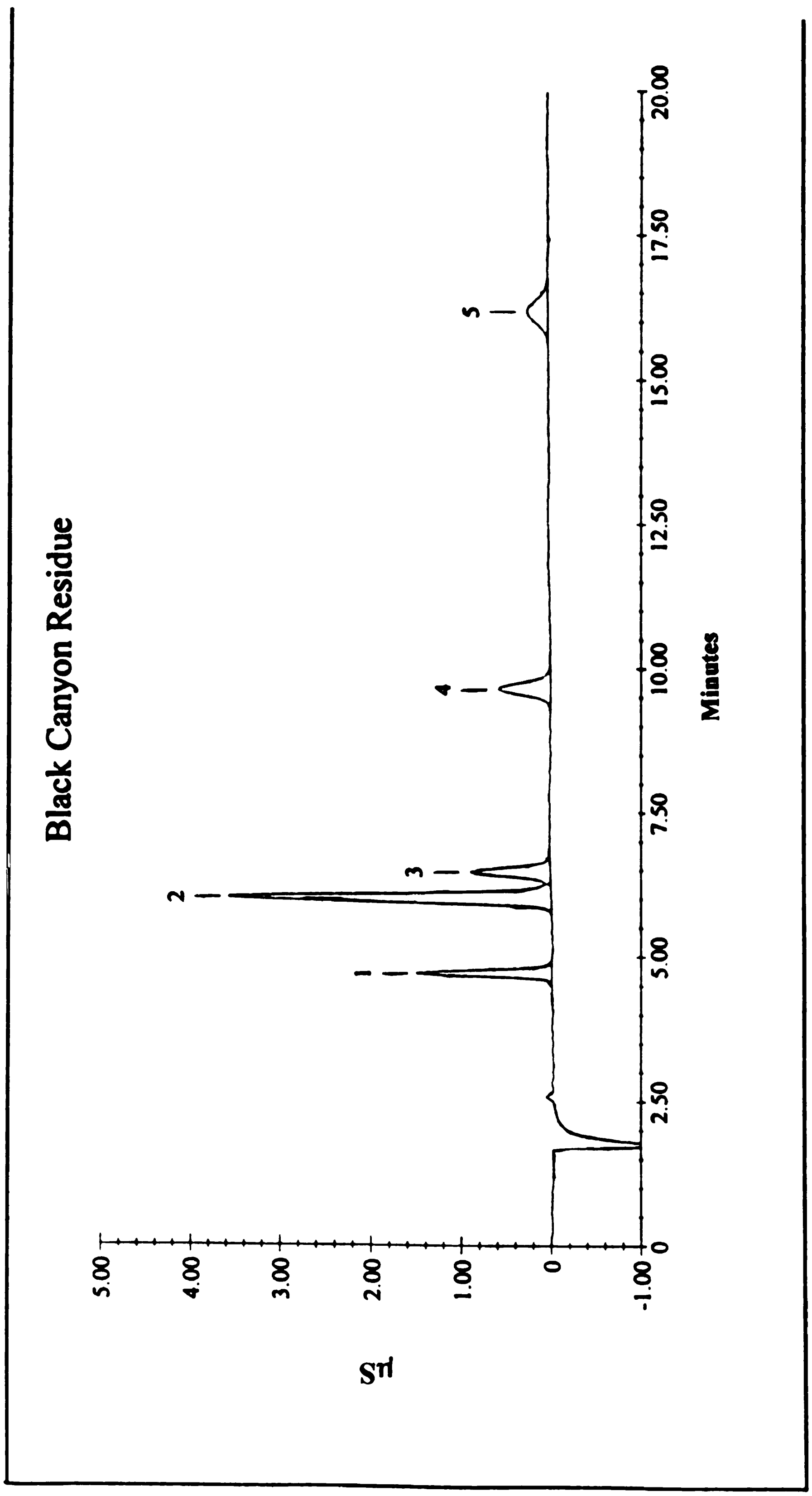
Peak #	Component Name	Retention Time	Amount (ppm)	Peak Area	Peak Height
1	NO_3	7.62	0.00	669807	84317
2		10.15	1.02	43977	2921
3		11.42	0.81	174778	13514


Black Canyon Residue
μS
10.0
8.0
6.0
4.0
2.0
0
-2.0
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
Minutes
1
2
3
5
6

CATION ANALYSIS REPORT OF RESIDUE

Sample Name: Black Canyon Residue

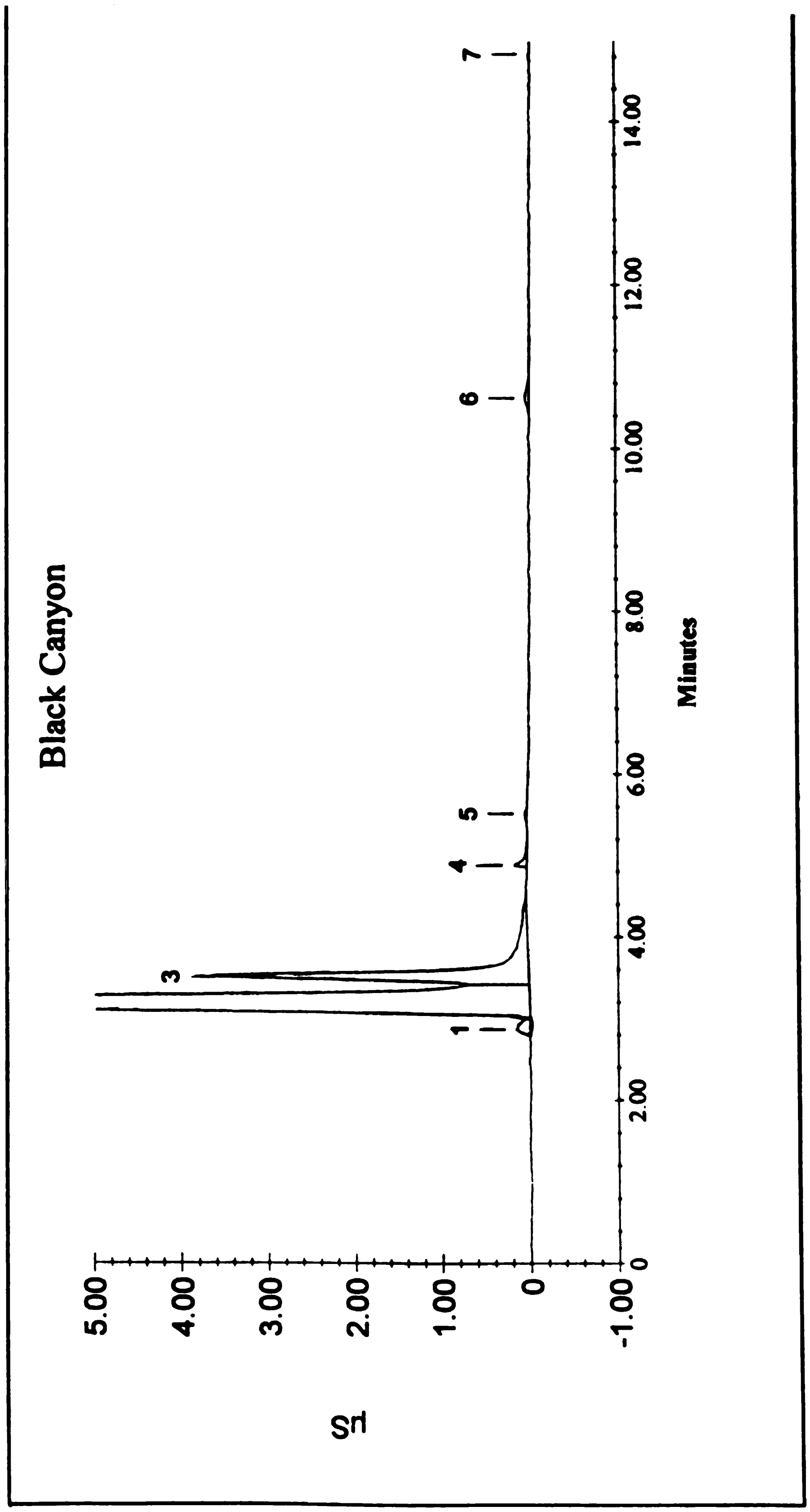
Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		2.47	659	103	6.43
2	Na	3.90	538069	63261	8.51
3	NH_4	4.50	92716	6112	15.17
4	K	5.60	3179898	215864	14.73
5	Mg	6.88	79429	3840	20.68
6	Ca	8.50	199314	9533	20.91


Black Canyon Residue
µS
5.00
4.00
3.00
2.00
1.00
0
-1.00
0
2.50
5.00
7.50
10.00
12.50
15.00
17.50
20.00
Minutes
1
2
3
4
5

ANION ANALYSIS REPORT OF RESIDUE

Sample Name: Black Canyon Residue

Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1	Cl	4.70	112315	14710	7.62
2	NO_2	6.00	352680	35377	9.97
3		6.47	99434	8923	11.14
4	NO_3	9.63	92382	5729	16.13
6		16.17	66263	2314	28.63

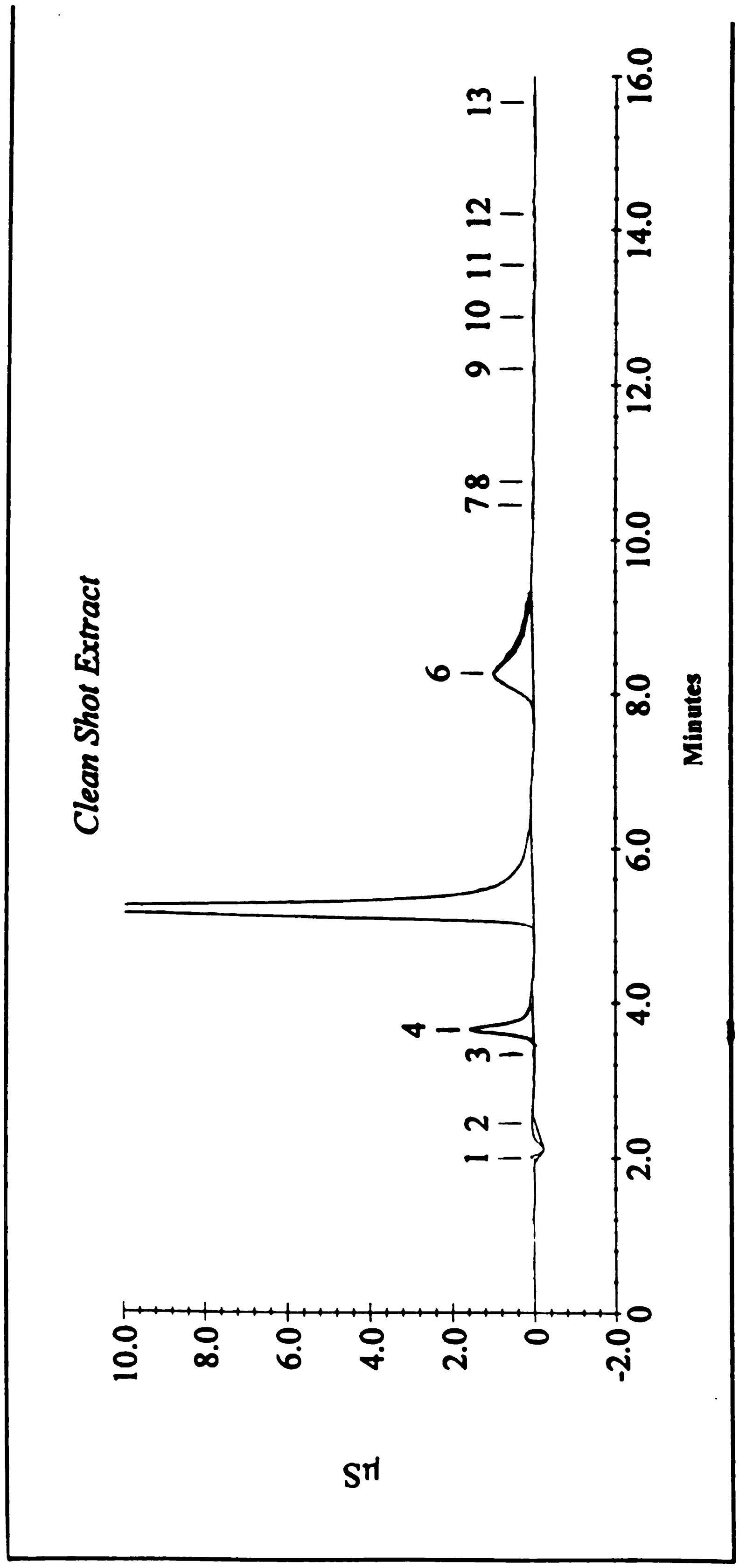


Black Canyon
µS
5.00
4.00
3.00
2.00
1.00
0
-1.00
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
Minutes
1
3
4
5
6
7

PERCHLORATE/THIOCYANATE REPORT

Sample Name: Black Canyon Residue

Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		2.87	12524	1641	7.63
2		3.17	1539251	175179	8.79
3		3.50	289557	34651	8.36
4		4.88	7646	1464	5.22
5		5.52	1508	251	6.00
6	ClO_4	10.62	7210	437	16.51
7		14.83	801	131	6.10

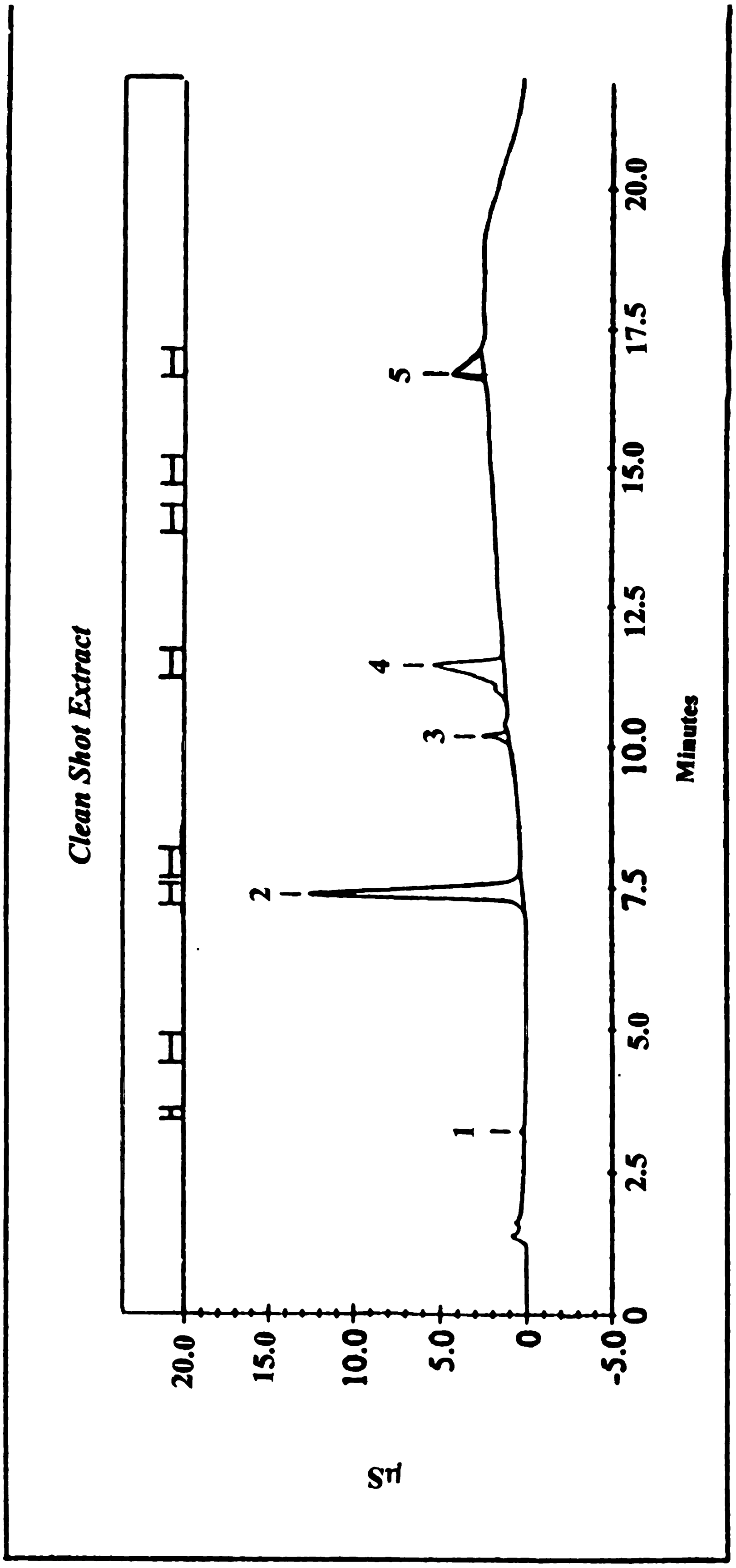


Clean Shot Extract
µS
10.0
8.0
6.0
4.0
2.0
0
-2.0
1 2
3
4
6
7 8
9 10 11 12
13
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
Minutes

CATION ANALYSIS REPORT OF EXTRACT

Sample Name: Clean Shot Extract

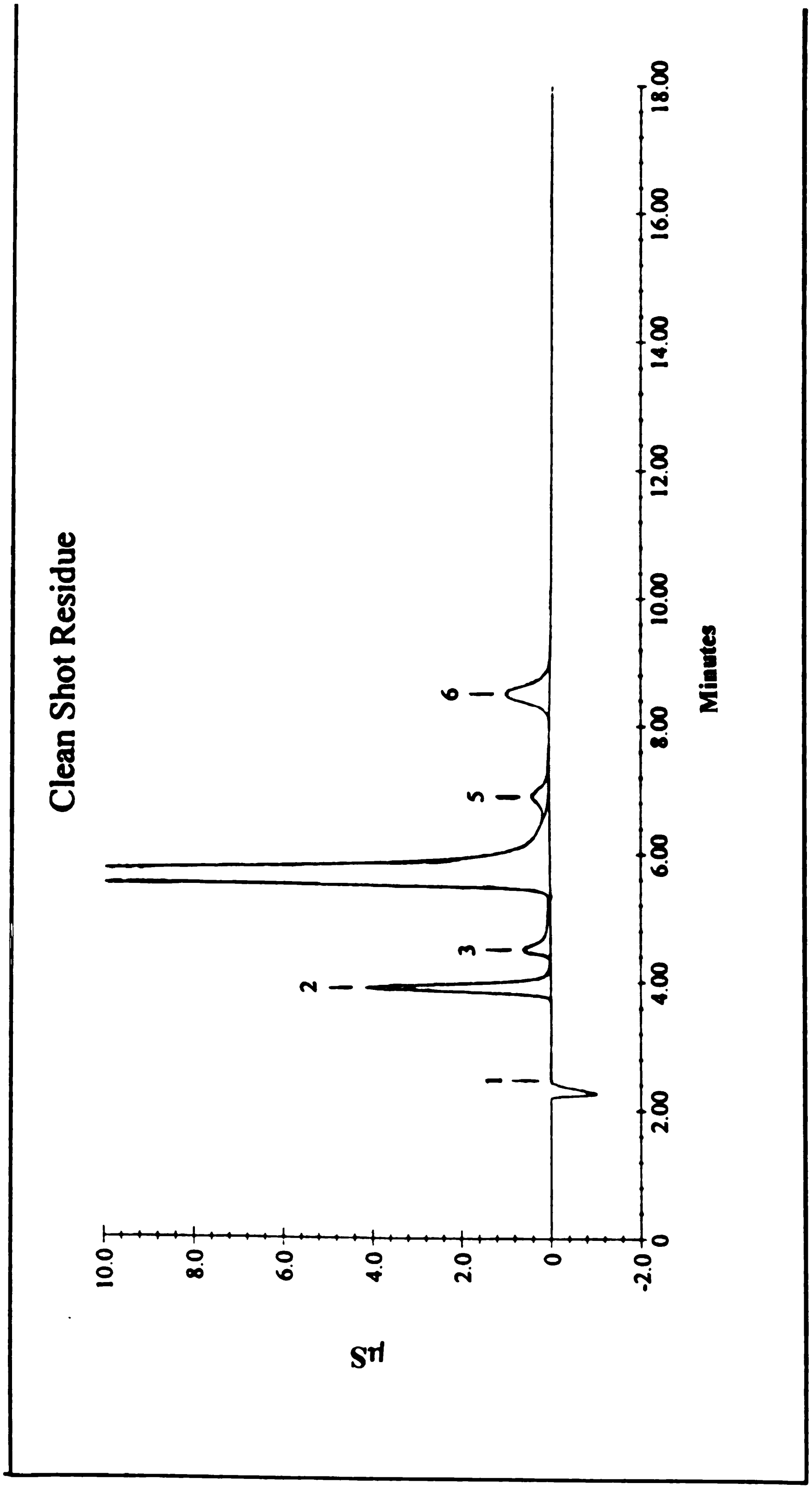
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1		2.00	0.00	7604	1549
2		2.45	0.00	23042	854
3		3.33	0.00	1225	195
4	Na	3.65	0.00	149532	15529
5	K	5.17	0.00	1657572	122569
6	Ca	8.27	0.00	334829	9703
7		10.45	0.00	2637	244
8		10.75	0.00	1384	218
9		12.20	0.00	2834	317
10		12.87	0.00	2001	208
11		13.53	0.00	2240	230
12		14.20	0.00	1343	235
13		15.65	0.00	6694	239


Clean Shot Extract
µS
20.0
15.0
10.0
5.0
0
-5.0
0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
Minutes
1
2
3
4
5

ANION ANALYSIS REPORT OF EXTRACT

Sample Name: Clean Shot Extract

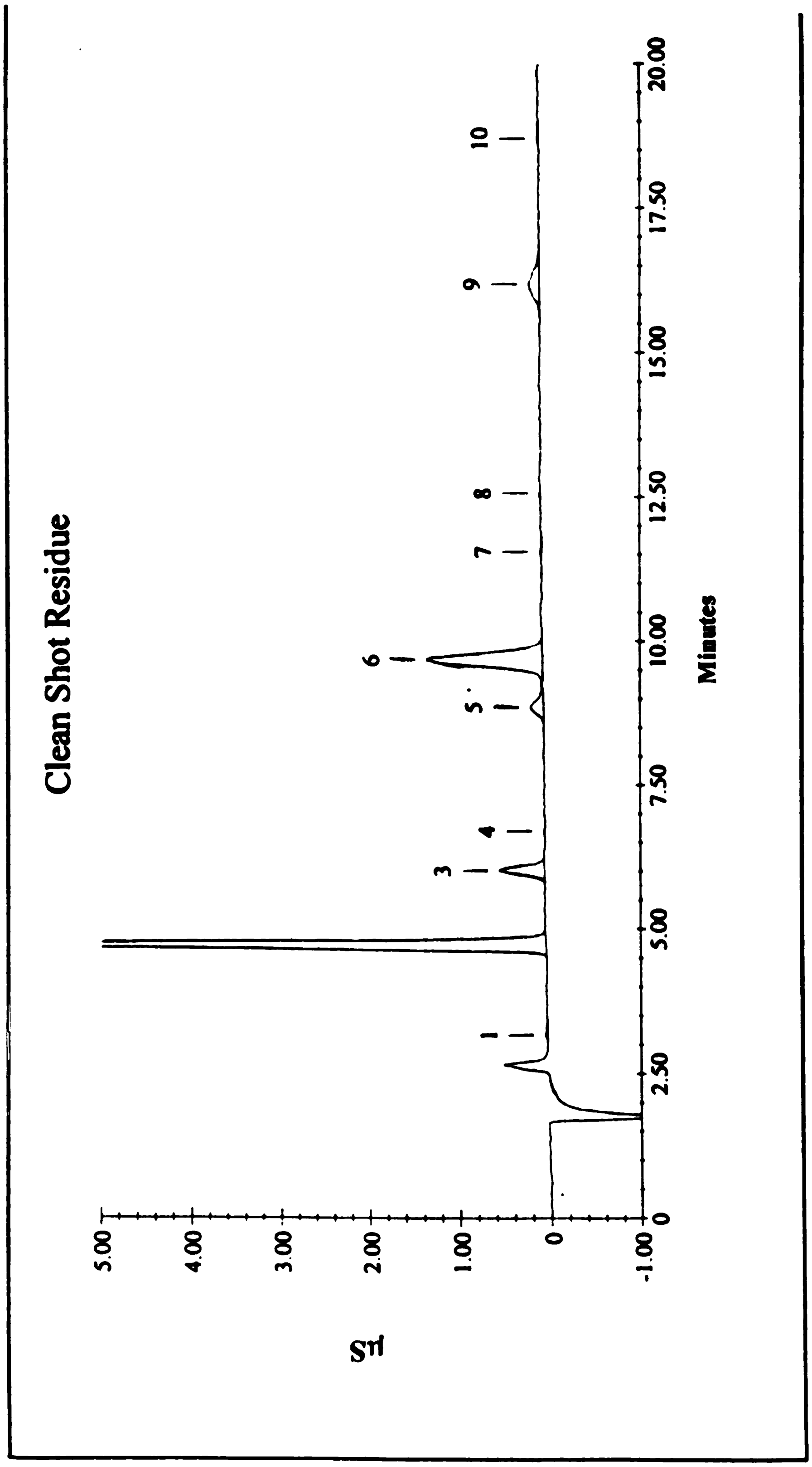
Peak #	Component Name	Retention Time	Amount (ppm)	Peak Area	Peak Height
1		3.22	0.00	.13924	2545
2	NO_3	7.37	0.00	1421300	123763
3		10.18	0.00	75069	14552
4	SO_4	11.45	3.21	689331	40913
5	ClO_4	16.70	34.98	322359	18336


Clean Shot Residue
μS
10.0
8.0
6.0
4.0
2.0
0
-2.0
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
Minutes
1
2
3
5
6

CATION ANALYSIS REPORT OF RESIDUE

Sample Name: Clean Shot Residue

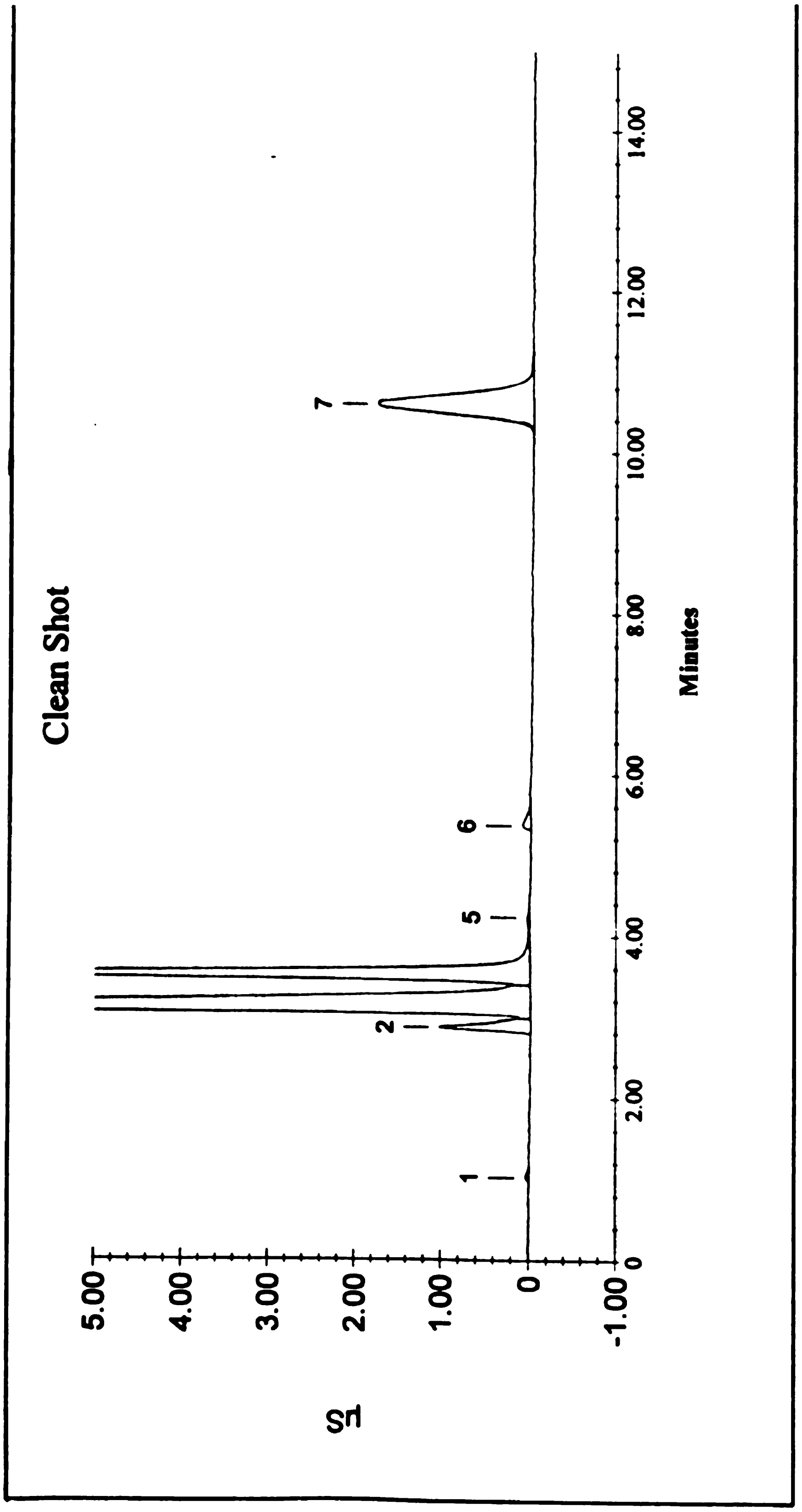
Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		2.47	2141	238	8.98
2	Na	3.90	355563	41897	8.49
3	NH_4	4.50	93413	6217	15.02
4	K	5.60	3190576	217325	14.68
5	Mg	6.90	73812	3660	20.16
6	Ca	8.50	208327	9921	21.00


Clean Shot Residue
µS
5.00
4.00
3.00
2.00
1.00
0
-1.00
0
2.50
5.00
7.50
10.00
12.50
15.00
17.50
20.00
Minutes
3
4
5
6
7
8
9
10

ANION ANALYSIS REPORT OF RESIDUE

Sample Name: Clean Shot Residue

Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		3.17	2511	255	9.85
2	Cl	4.72	587058	79284	7.40
3	NO_2	6.02	48948	5001	9.79
4		6.70	1142	151	7.57
5	ClO_3	8.85	23742	1428	16.63
6	NO_3	9.67	198273	12757	15.54
7		11.55	2035	198	10.28
8		12.57	717	114	6.28
9		16.18	35651	1169	30.51
10		18.70	1956	153	12.77


Clean Shot
µS
5.00
4.00
3.00
2.00
1.00
0
-1.00
Minutes
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
1
2
5
6
7

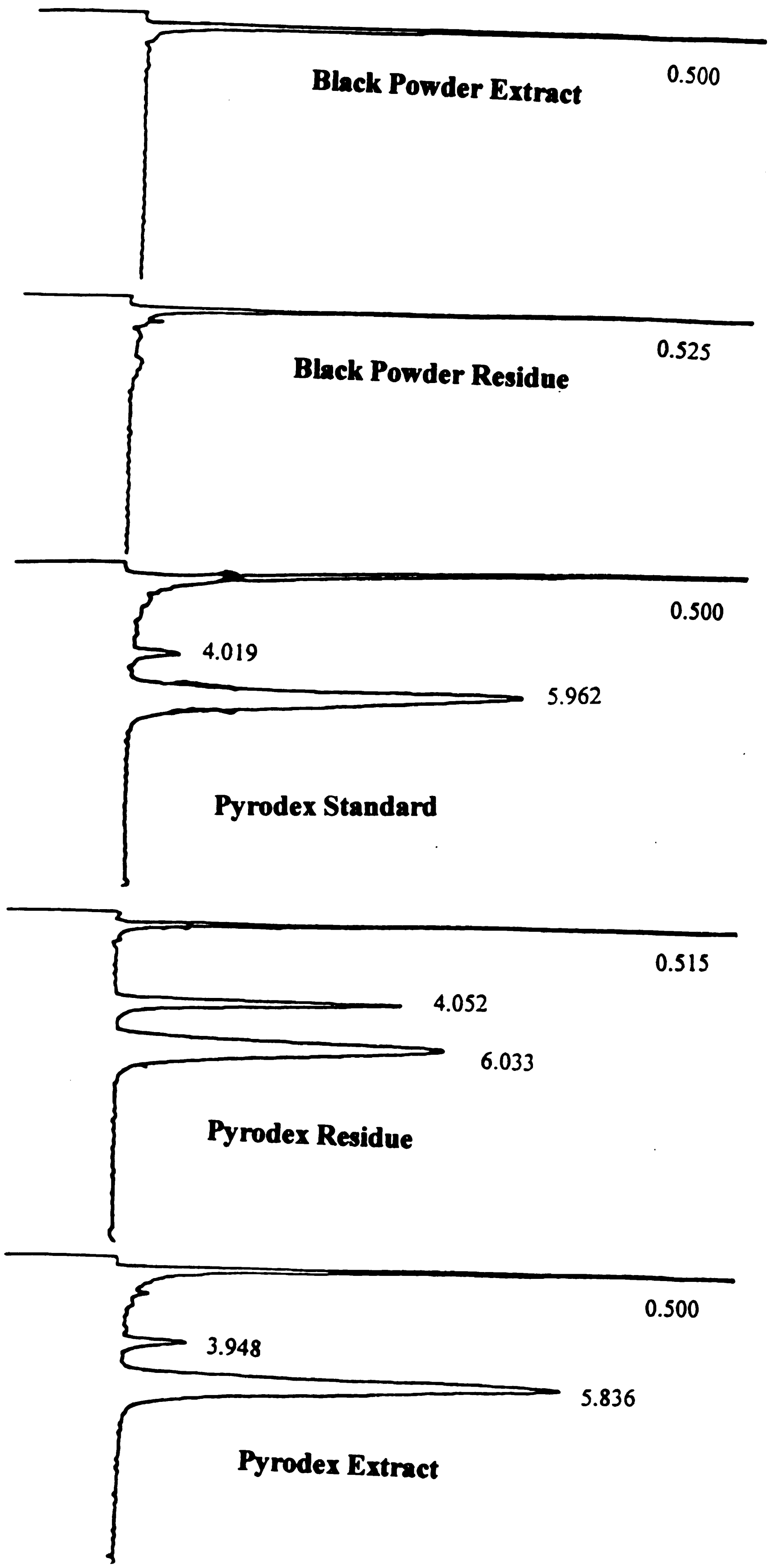
PERCHLORATE/THIOCYANATE REPORT

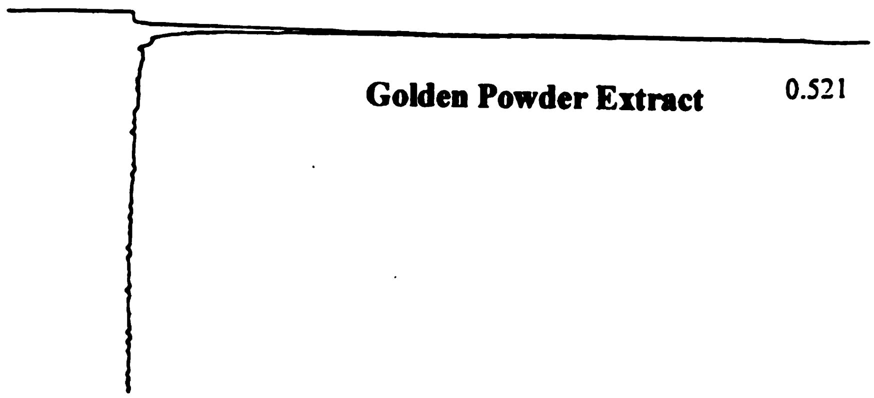
Sample Name: Clean Shot Residue

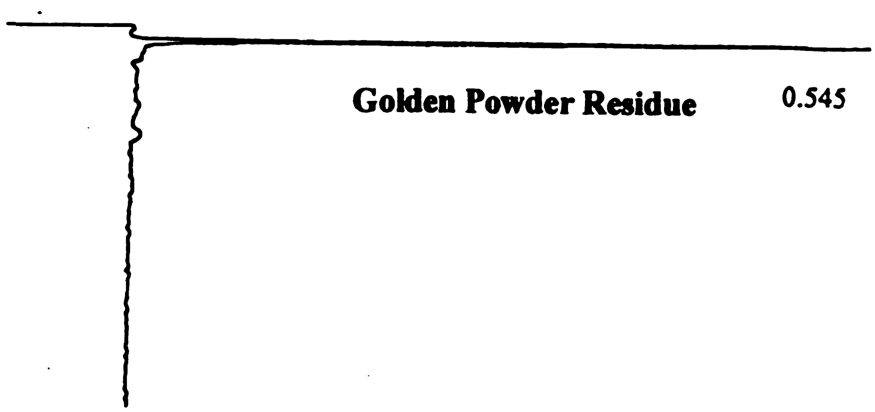
Peak #	Component Name	Retention Time	Peak Area	Peak Height	Area/Height Ratio
1		1.02	2649	406	6.53
2		2.87	59332	10309	5.76
3		3.10	1290051	190735	6.76
4		3.50	499143	72055	6.93
5		4.23	1928	221	8.74
6		5.37	9296	938	9.91
7	ClO_4	10.58	296327	17830	16.62

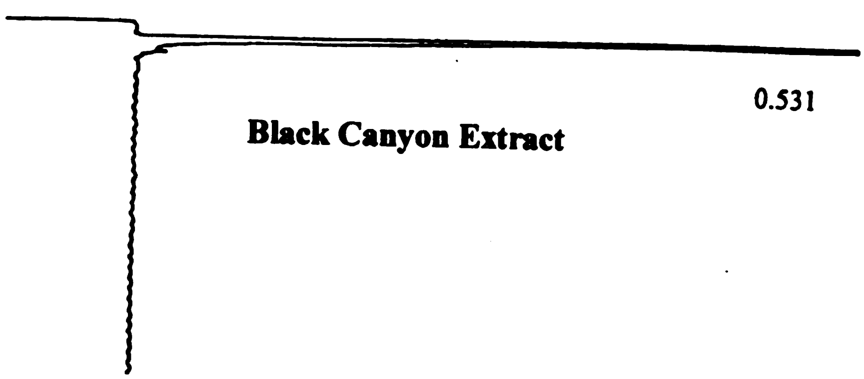
APPENDIX V

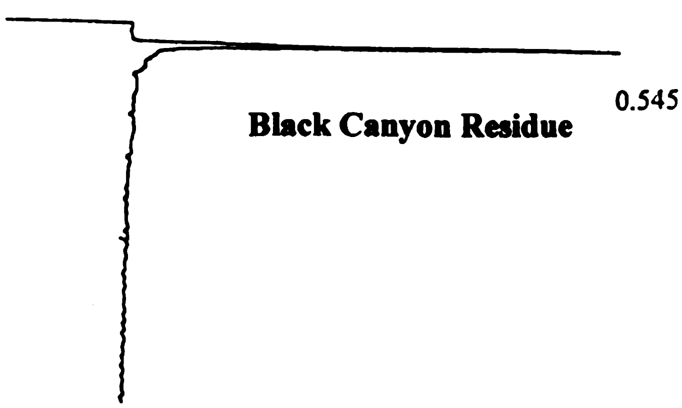
HPLC Results

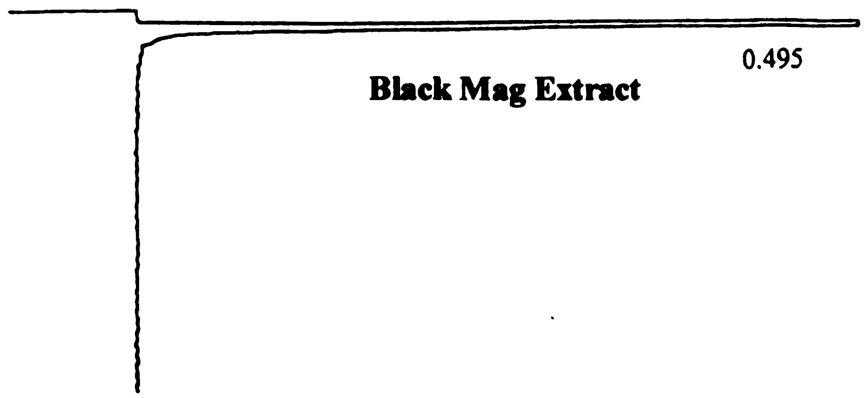

0.500
Black Powder Extract
0.525
Black Powder Residue
0.500
4.019
5.962
Pyrodex Standard
0.515
4.052
6.033
Pyrodex Residue
0.500
3.948
5.836
Pyrodex Extract

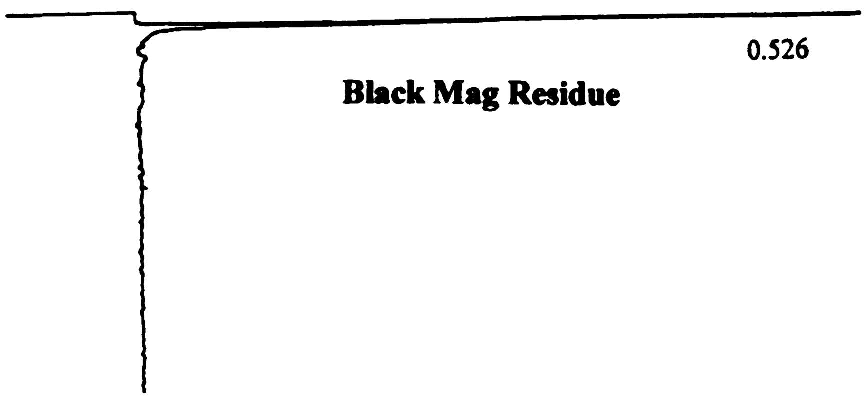

Golden Powder Extract
0.521

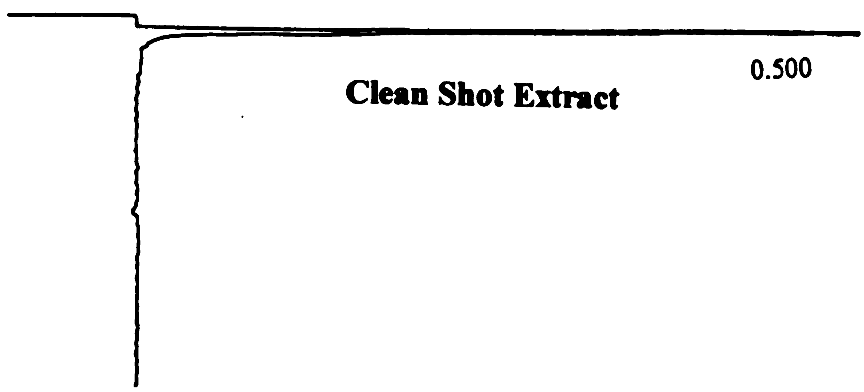

Golden Powder Residue
0.545

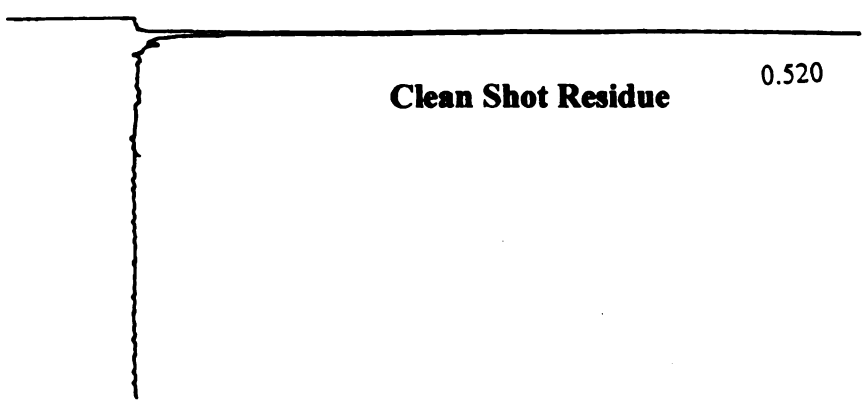

0.531
Black Canyon Extract


0.545
Black Canyon Residue


0.495
Black Mag Extract


0.526
Black Mag Residue


0.500
Clean Shot Extract


0.520
Clean Shot Residue

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