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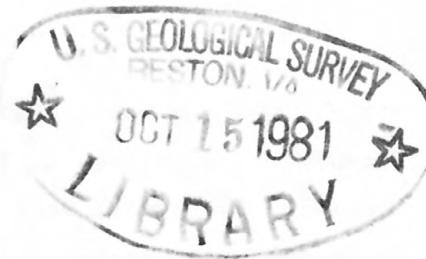
1 United States Department of the Interior  
2 Geological Survey

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7 Analysis of Egyptian Geological Survey and Mining Department samples  
8 by rapid rock and atomic absorption procedures

9 by

10 Jean S. Kane and Hezekiah Smith

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Hezekiah ✓



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15 Open-file report  
16 United States  
17 Geological Survey  
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19 Open-File Report 81-991

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21 This report is preliminary and has not been  
22 reviewed for conformity with U.S. Geological  
23 Survey editorial standards and stratigraphic  
24 nomenclature. Any use of trade names is for  
25 descriptive purposes only and does not imply  
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## INTRODUCTION

A suite of 165 samples from the Egyptian Geological Survey and Mining Department was analyzed for several elements in the Branch of Analytical Laboratories (BAL) of the U.S. Geological Survey by M. Iskander and S. Holyle during training here that focused on rapid-rock analytical procedures and on atomic-absorption spectrometric analyses. Because the training period was too brief to complete all required analyses on these samples, members of the BAL did additional determinations. These materials will serve as control samples when the newly learned techniques are implemented at the Cairo laboratory by M. Iskander and S. Holyle.

This open file report summarizes the results of analysis for rapid rock procedures used to determine  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{MnO}$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}^+$ , and  $\text{H}_2\text{O}^-$  (H. Smith), and for flame and electrothermal atomic absorption spectrometric determinations of Cu, Zn, Ni, Co, V, Cr, Cd, Ba, and Sr (J. Kane). Additionally, all procedures used for the AAS analyses are included in this report. These procedures are somewhat specific to the particular instrumentation used, which is essentially the same as that being purchased by the Egyptian Geological Survey and Mining Department. The Perkin-Elmer HGA 500 graphite furnace especially differs considerably in operating procedure from earlier models and is sufficiently new that literature references to HGA determinations of specific elements give inapplicable instrumental parameters. In the case of the rapid rock analyses excepting  $\text{CO}_2$ , S, and  $\text{PO}_4^{=}$ , procedures are documented quite adequately in U.S. Geological Survey Bulletin 1401, Rapid Analysis of Silicate, Carbonate, and Phosphate Rocks - Revised Edition, 1975.

$\text{CO}_2$  was determined colorimetrically with a  $\text{CO}_2$  analyzer on 100mg. of sample. Sulfur was determined on a Leco SC-132(IR) analyzer. Phosphate was determined spectrophotometrically at 420 nm as the molybdovanado phosphoric acid complex after fusing the sample with a lithium metaborate-lithium tetraborate mixture.

Semiquantitative emission spectroscopy (SQS) analyses on these samples (J. Harris and others, 1981) have been summarized in a separate open file report.

### The Samples

The samples analyzed fall into 10 subgroups. Sixty six syenites were collected from three locations. Of these, samples 1S - 30S are from Gabal Mishbih at latitude 22°44', longitude 34°43'; 31S - 50S are from Gabal Nigrub El Tahtani at latitude 23°01', longitude 35°02'; and 51S - 66S are from Gabal Maladob at latitude 22°44', longitude 34°50'.

Five of the subgroups were collected in the Umm Gheig lead-zinc mine located at latitude 25°43', longitude 34°15'. These include conglomerates C1 to C10, clays CL1 to CL10, gypsums G1 to G10, oil tainted limestones OL1 to OL10, and lime grits LG1 to LG10.

Metamorphic rocks included greywackes, samples 1M - 16M and siltstones 17M - 29M from the Wadi Hammamat at latitude 25°58', and longitude 33°33'.

Sulfide ores were collected from three localities, samples Darahib 1 - 5 from the Darahib talc mine at latitude 24°01', longitude 35°01'; samples 1 - 7 from eastern emine, Umm Samiuki copper-zinc deposit at latitude 24°14', longitude 34°49'; sample 1 Maakal from an occurrence just east of Umm Samiuki; and samples Hamata 1 - 2 from the Hamata talc mine at latitude 24°15'30", longitude 35°13'.

Additionally, three phosphate ores were analyzed.

Experimental: Atomic Absorption Spectrometric Analyses

Sample dissolution-all samples except sulfides: 500mg samples were weighed into teflon beakers to each of which 2ml  $\text{HNO}_3$ , 3ml  $\text{HClO}_4$ , and 10ml HF were added. (All acids were concentrated reagent grade.) The samples were heated in open beakers at  $150^\circ\text{C}$  on a hotplate overnight. To each resulting dry residue, 2.5ml HCl was added and the sides of the beakers were rinsed with a small volume of distilled water before warming the beakers gently to dissolve salts. The solutions were transferred to linear polyethylene 50ml volumetric flasks and diluted to volume.

Concentration in Solution  $\times 100$  = Concentration in sample.

Sample dissolution-sulfide ores: 100mg samples were weighed into teflon beakers to which 10ml HCl, 3ml  $\text{HClO}_4$ , and 10ml HF were added. (All acids were concentrated reagent grade.) The samples were heated uncovered on a hot plate for 1 hour at  $200^\circ\text{C}$ , then cooled slightly off the hot plate before adding 2ml  $\text{HNO}_3$ . The samples were then heated to heavy fumes of  $\text{HClO}_4$ , reducing acid volume to 3ml or less. After cooling off the hotplate for about 10 min. 2 ml  $\text{HNO}_3$  and 5ml HCl were added to the samples and they were evaporated to dryness of  $200^\circ\text{C}$  overnight, baking the solid residue thoroughly. After brief cooling the residue was dissolved by adding 2.5ml HCl to the beakers, and rinsing the sides with a small (5ml) volume of distilled water, and gently warming. The clear solutions were transferred to 50 ml linear polyethylene volumetric flasks and filled to volume. Concentration in solution  $\times 500$  = Concentration in sample.

Instrumentation: All flame atomic absorption measurements were made using a Perkin Elmer 5000 atomic absorption spectrophotometer equipped with deuterium arc and tungsten iodide background correction. All electrothermal atomization atomic absorption

measurements were performed using the Perkin Elmer HGA 500 graphite furnace in conjunction with a Perkin Elmer 603 spectrophotometer and an AS 50 Autosampler. The spectrophotometer was equipped with deuterium arc background correction, and with a Perkin Elmer model 56 strip chart recorder. Argon was used as the purge gas.

The light source for each element was a hollow cathode lamp, operated at the lamp current recommended on the individual lamp labels. Note, however, that as the background corrector deuterium arc lamp loses intensity with age, V and Cr hollow cathode lamps must be operated at less than the recommended lamp current in order to balance their intensities with that of the deuterium arc.

Instrumental parameters for each of the elements follow. Table Ia lists flame conditions while Table Ib lists those for the graphite furnace. Tables IIa-b list detection limits, analytical sensitivities, and the upper limit of linearity in the absorbance vs. concentration calibration plots for the analyses performed. Detection limits are a function of solution concentration, and can be improved where necessary by decreasing the digestion dilution factor. For furnace analyses they can also be improved by injecting a larger sample aliquot up to 50  $\mu$ l. Longer drying and charring hours on the order of 40-50 sec. then become necessary.

Table Ia

## OPERATING PARAMETERS: FLAME ATOMIZATION

Element	Wavelength nm	Band Pass nm	Background Correction	Burner Head Rotation	Flame Type*
Cu	324.7	.7	No	Yes-60°	lean air-acet.
	324.7	.7	No	No	lean air-acet.
	222.6	.2	Yes	No	lean air-acet.
Zn	213.9	.7	Yes	Yes-60°	lean air acet.
	213.9	.7	Yes	No	lean air-acet.
Ni	232.0	.2	Yes	No	lean air-acet.
Cd	228.8	.7	Yes	No	lean air-acet.
Cr	357.9	.7	Yes	No	rich air-acet.
	357.9	.7	Yes	No	rich $N_2O_2$ -acet.
Ba	553.6	.14	No	No	rich $N_2O_2$ -acet.
Sr	460.7	1.4	No	No	rich air-acet.

Any single absorbance output was obtained by averaging three absorbances, each integrated over three seconds.

\*The term "lean" implies that the flame was fuel-lean, i.e., the fuel-to-oxidant ratio was substoichiometric. Conversely, the term "rich" implies that the flame was fuel-rich, i.e., the fuel-to-oxidant ratio was superstoichiometric.

TABLE Ib

## OPERATING PARAMETERS: GRAPHITE FURNACE ATOMIZATION

Sample Size: 20  $\mu$ l injected using AS 50 autosampler

Purge Gas: Argon

Peak Height Mode

Element	Wavelength nm	Slit mm	Tube Type	HGA 500-Program Sequence
Ni	232.0 <sup>1</sup>	.2	pyrolytic graphite	Step 1: Dry at 100°C, ramp 10 s and hold 10 s  Step 2: Char at 1000°C, ramp 10 s and hold 10 s  Step 3: Atomize at 2300°C maximum power (0 ramp) hold 7 s; interrupt gas flow to 50ml/min; -10 record, -7 baseline  Step 4: Cool to 100°C, ramp 10 s
Co	240.7 <sup>2</sup>	.2	pyrolytic graphite	Step 1: Dry at 100°C, ramp 10 s and hold 10 s  Step 2: Char at 1000°C, ramp 10 s and hold 10 s  Step 3: Atomize at 2200°C, maximum power, hold 7 s; interrupt gas flow to 50ml/min; -10 record, -7 baseline  Step 4: Cool to 100°C, ramp 10 s  Step 5: Clean tube: 2500°C maximum power, hold 4 s  Step 6: Cool to 100°C, ramp 10 s

<sup>1</sup>Be sure to avoid non-absorbing 231.7nm line.<sup>2</sup>Avoid less sensitive 241.2nm line

Element	Wavelength	Slit	Tube Type	HGA 500-Program Sequence
	nm	mm		
Cr	357.9	.7	pyrolytic graphite	<p>Step 1: Dry at 100°C, ramp 10 s and hold 10 s</p> <p>Step 2: Char at 1200°C, ramp 10 s and hold 10 s</p> <p>Step 3: Atomize at 2300°C maximum power, hold 7 s; interrupt gas flow to 50ml/min; -10 record, -7 baseline</p> <p>Step 4: Cool to 100°C, ramp 10 s</p> <p>Step 5: Clean tube: 2500°C maximum power, hold 4 s</p> <p>Step 6: Cool to 100°C, ramp 10 s</p>
V	318.4	.7	pyrolytic graphite	<p>Step 1: Dry at 100°C, ramp 10 s and hold 10 s</p> <p>Step 2: Char at 1500°C, ramp 10 s and hold 10 s</p> <p>Step 3: Atomize at 2700°C maximum power, hold 7 s; interrupt gas flow to 50ml/min; -10 record, -7 baseline</p> <p>Step 4: Cool to 100°C, ramp 10 s</p> <p>Step 5: Clean tube: 2600°C maximum power, hold 4 s</p> <p>Step 6 Cool to 100°C, ramp 10 s</p>
Cd	228.8	.7	regular graphite	<p>Step 1: Dry at 100°C, ramp 10 s and hold 10 s</p> <p>Step 2: Char at 250°C, ramp 10 s and hold 10 s</p> <p>Step 3: Atomize at 2100°C, ramp 1 s and hold 6 s; interrupt gas flow to 0ml/min; -10 record, -7 baseline</p>

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Table IIa

Flame Atomic Absorption Sensitivities and Detection Limits

Element	Operating Parameters	Sensitivity ug/ml	Detection Limit ug/ml	Linear Range ug/ml
Cu	lean air-acet.; 324.7nm; straight burner	.069	.02	0-5.0
	lean air-acet.; 324.7nm; 60° rotation of burner	1.10	.20	10-300
	lean air-acet.; 222.6nm; straight burner	2.0	1.0	10-100
Zn	lean air-acet.; 213.9nm;BG; straight burner	.015	.013	0-2.0
	lean air-acet.; 213.9nm;BG; 60° rotation of burner	.45	.10	10-20.
Ni	lean air-acet.; 232.0nm;BG; straight burner	.14	.06	0-7.0
Cd	lean air-acet.; 228.8nm;BG; straight burner	.020	.025	0-2.0
Cr	lean air-acet.; 357.9nm; straight burner	1.10	.43	0-2.0
	rich air-acet.; 357.9nm; straight burner	.073	.016	0-1.0
	rich $N_2O_2$ -acet.; 357.9nm; straight burner	.26	.14	0-2.0

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Table IIb

Graphite Furnace Atomic Absorption Sensitivities and Detection Limits

Element	Operating Parameters see Table Ib	Sensitivity ng/ml	Detection Limit ng/ml	Linear Range ng/ml
Cr	357.9 nm; max. power atomization at 2300°C	2.0	.10	0-100
Cd	228.8 nm; 1 sec. ramp atomization at 2100°C	.065	.05	0-70
Co	240.7 nm; max power atomization at 2200°C	1.4	.95	0-70
Ni	232.0 nm; max. power atomization at 2300°C	.90	3.0	0-100
V	318.4 nm; max. power	8.0	30.0	0-700

Cd extraction: Prepare 5 Cd standard solutions covering the analytical range (generally 1 ng ml<sup>-1</sup> to 15 ng ml<sup>-1</sup>) by dilution from a 100 ppm stock solution into 5% (v/v) HCl. It is advisable to extract a standard blank, a sample digestion blank, and 4-5 standards with each set of 10-12 unknowns. Experience may indicate no significant difference between the two blanks, in which case one may be omitted. Pipette into the separatory funnels 5ml aliquots of the blank and standards, and an appropriate aliquot of unknown as discussed immediately following the extraction procedure. Add 5% (v/v) HCl to complete a 5ml aliquot volume. Add to each 0.5ml of 20% hydroxylamine hydrochloride, 5ml 10% (w/v) sodium potassium tartrate, and 5ml 10% (w/v) sodium hydroxide. Add 15ml 0.1% (w/v) dithizone in xylene and mix 5 minutes using air bubblers or a mechanical shaker. Allow layers to separate. Color in upper organic layer will range from very pale straw through pink to an almost black purple depending on amounts of Zn, Pb, and Mn which coextract with the Cd. The aqueous layer should be very orange.

Remove and discard the aqueous phase. Wash the organic phase twice with 5ml of 0.1% (v/v) ammonium hydroxide, mixing about 1 minute each time and discarding the aqueous wash.

Add 5ml 5% (v/v) HCl to the organic layer and mix 10 minutes with an air bubbler or mechanical shaker to back extract the Cd into the aqueous phase. After rinsing and drying the separatory funnel stems, collect the aqueous phase for atomic absorption measurement.

NOTE: The extraction time of 5 minutes and the stripping time of 10 minutes are the optimum for constant extraction yields between samples and aqueous standards. Reproduceability of results from one extraction run to another requires attention to careful timing of these steps.

Inject 20ul aliquots, preferably using autosampler AS 50, into a regular graphite tube and atomize as indicated in the previous table of furnace conditions.

Determination of Appropriate Aliquot for Cd Extraction:

Most frequently, sample digestions are a factor of 100 more dilute than the solids samples, and the extraction is done using a 2.5ml aliquot of sample, which after extraction is stripped to 5ml. For those samples at crustal abundance levels to a factor of 10 higher, this final solution falls within the ideal concentration range for graphite furnace analyses. Using these volumes

$$\text{PPM in Stripped Solution} \times 200^1 = \text{PPM in Sample.}$$

The sulfide samples contained very much higher Cd levels, high enough for the digests to be above the 0.10ppm lower limit for flame analyses. Since adequate background correction is problematic for Cd without separation, the flame determination was used to only estimate Cd levels for selection of the appropriate extraction aliquot. Above 0.015ppm, the graphite furnace peak height vs. concentration calibration plot is unusable because of severe curvature. To reduce the original digest solution concentrations to below this high curvature region, 50ul was extracted and then stripped to a 10ml volume. For this case,

$$\text{PPM in Stripped Solution} \times 100,000^2 = \text{PPM in Sample}$$

For those samples whose Cd concentration is below flame detection limits, the 2.5ml extraction aliquot stripped to 5ml is best. The stripped solution may well have a concentration between the furnace analysis upper limit of 0.015ppm and the flame analysis lower limit but can be diluted in this case after extraction.

<sup>1</sup> digestion factor (=100) x extraction factor (=2) = 200

<sup>2</sup> digestion factor (=500) x extraction factor (=200) = 100,000

Discussion of Results:

Flame Atomic Absorption Measurements: Mixed standards were prepared to contain Cu, Zn, Cd, Cr, and Ni in 5% HCl for atomic absorption calibration. A series of 5-10 standards was used to cover the entire analytical range and to fully define any curvature of the calibration plot within that range. Aliquots of the sample digests were made 0.5% (w/v) in both Na and La for the Ba and Sr determinations, and mixed standards were prepared in the same matrix. The La mitigates against Sr suppression caused by Al and Si while Na acts as an ionization buffer.

Analytical sequences typically included the 5-10 calibration standard solutions, plus a blank, the unknowns (90 of the 165 samples were analyzed after the training program ended), and 3-5 standard rock digests. Absorbance measurements were made using 3 second integration times, averaging three such measurements for a single reported absorbance. Absorbances for each of the calibration standards and standard rock solutions were read at least three times during the run. Absorbance measurements for these standards were read as a group at the start and at the completion of a run; additionally, the absorbance measurements for the standards were interspersed among those for the unknown samples, and absorbance measurements of both were read in this randomized sequence. This procedure allowed identification of and correction for any baseline drift or sensitivity change occurring during the run. Generally such drift was small and consequently not a concern.

For Cu, all sample types except the sulfide ores had Cu concentrations within the range 1ppm-150ppm, and could be analyzed at the usual absorbing line of 324.7nm. For the sulfides, the use of this

line required reduction of sensitivity by 60° burner rotation or by the use of the 222.6nm line. A 1/50 dilution eliminated need for reduced sensitivity. Mn nodules A-1 and P-1 were the only standard samples whose Cu concentrations were high enough to check accuracy of analysis with the Cu 222.6nm line. The matrix mismatch between ferromanganese oxides and sulfide ores is undesirable, however. As the data of Table III show, analyses with and without dilution are in excellent agreement. This comparison suggests that dilution, a time-consuming step with the potential for introducing both volume and contamination errors, is unnecessary.

Several of the sample subgroups, conglomerate, clay, lime grit, limestone, and sulfides also required burner rotation for the determination of Zn. Maximum ninety-degrees rotation reduces sensitivity by about a factor of 10; this was insufficient for the sulfide ores which required both rotation and a 1/50 dilution. Zn has only one alternate absorption line at 307.6nm that provides a factor of 4700 sensitivity reduction. Since a factor of 500 reduction was needed for the Zn analysis in the sample, dilution was unavoidable.

Cd determinations without prior separation are not possible on the graphite furnace. However, the interferences in flame determinations are far less severe, and preliminary flame analysis enables the determination of a proper extraction aliquot when the added accuracy of the extraction procedure with the subsequent determination by graphite furnace atomization is required. The comparison of results from the two procedures in Table IV indicates suppression of Cd by matrix interferents of about 20% for flame analysis without prior separation.

TABLE III

Comparison of Cu Determinations After Sensitivity Reduction by  
 1) Rotation of Burner Head and 2) Sample Dilution

<u>Sample</u>	<u>Cu Concentration, ppm</u>		
	<u>Burner Rotation</u>	<u>Dilution</u>	<u>Literature</u>
Sulfide Ore 1	25,200	24,100	-
	2	107,000	-
	9	13,900	-
	11	120,000	-
Mn Nodules A-1	1,160	-	1,100 <sup>1</sup>
P-1	11,500	-	11,600 <sup>1</sup>

One figure more than the significant two figures is shown in this table for purposes of comparison only.

<sup>1</sup>USGS Prof. Paper 1155, F. J. Flanagan and David Gottfried, 1980,  
 U.S. Government Printing Office, Washington, DC, pp. 37, 39.

Table IV

Cd Determinations With and Without Prior Extraction

<u>Sample</u>	<u>Cd Concentration, ppm</u>	
	Flame Atomization, no extraction	HGA Furnace Atomization, after extraction
Sulfide Ore 3	550	650
5	700	720
8	870	970
10	210	260
11	150	170
12	350	420
13	1000	1300

While chromium has been widely determined in a variety of materials by flame atomic absorption, difficulties are experienced when the determination is made in an air-acetylene flame. Sensitivity for Cr is best when the flame is fuel-rich; however, iron and nickel both significantly suppress chromium absorption in such a flame (Slavin, 1968).

This suppression can be compensated for in a variety of ways, including the use of the hot lean air-acetylene flame (Dyck, 1965), use of the hotter and more oxidizing nitrous oxide-acetylene flame (Techtron, 1972), and method of additions.

Table V shows the comparison between analytical results employing these options for several samples in the flame analytical range, including the NBS coal ash standards 1633 and 1633a. While these in no way duplicate the matrix of the clays, phosphates, greywackes, or siltstones, they are the only available standards for which Cr falls in the appropriate concentration range. Comparison of the analytical results with the certified values for standard reference materials shows acceptable agreement for all methods. The extremely poor sensitivity of the lean air-acetylene flame measurement nonetheless makes its use undesirable. Cr analyses for the EGS samples were done using a rich air-acetylene flame.

Table V

Comparisons of Cr Concentrations  
Determined by Several Analytical Procedures

Sample	Cr concentration, ppm, determined <u>directly from calibration curve</u>		by method of additions	
	lean air-acet.	rich air-acet.	rich $N_2O_2$ -acet.	rich air-acet.
Phosphate 1		55	54	
Clay	1	128	135	130
	2	137	151	146
	9	132	128	141
	10	123	121	127
Siltstone 17		135		135
	19	144		139
NBS				
Coal Ash 1633 <sup>1</sup>	149	151	163	154
NBS				
Coal Ash 1633a <sup>2</sup>	216	200	203	

One figure more than the two significant figures is shown in this table for comparison only.

<sup>1</sup>Cr 131 ppm 1974 Certificate of Analysis, National Bureau of Standards  
<sup>2</sup>Cr 196 ppm 1979 Certificate of Analysis, National Bureau of Standards

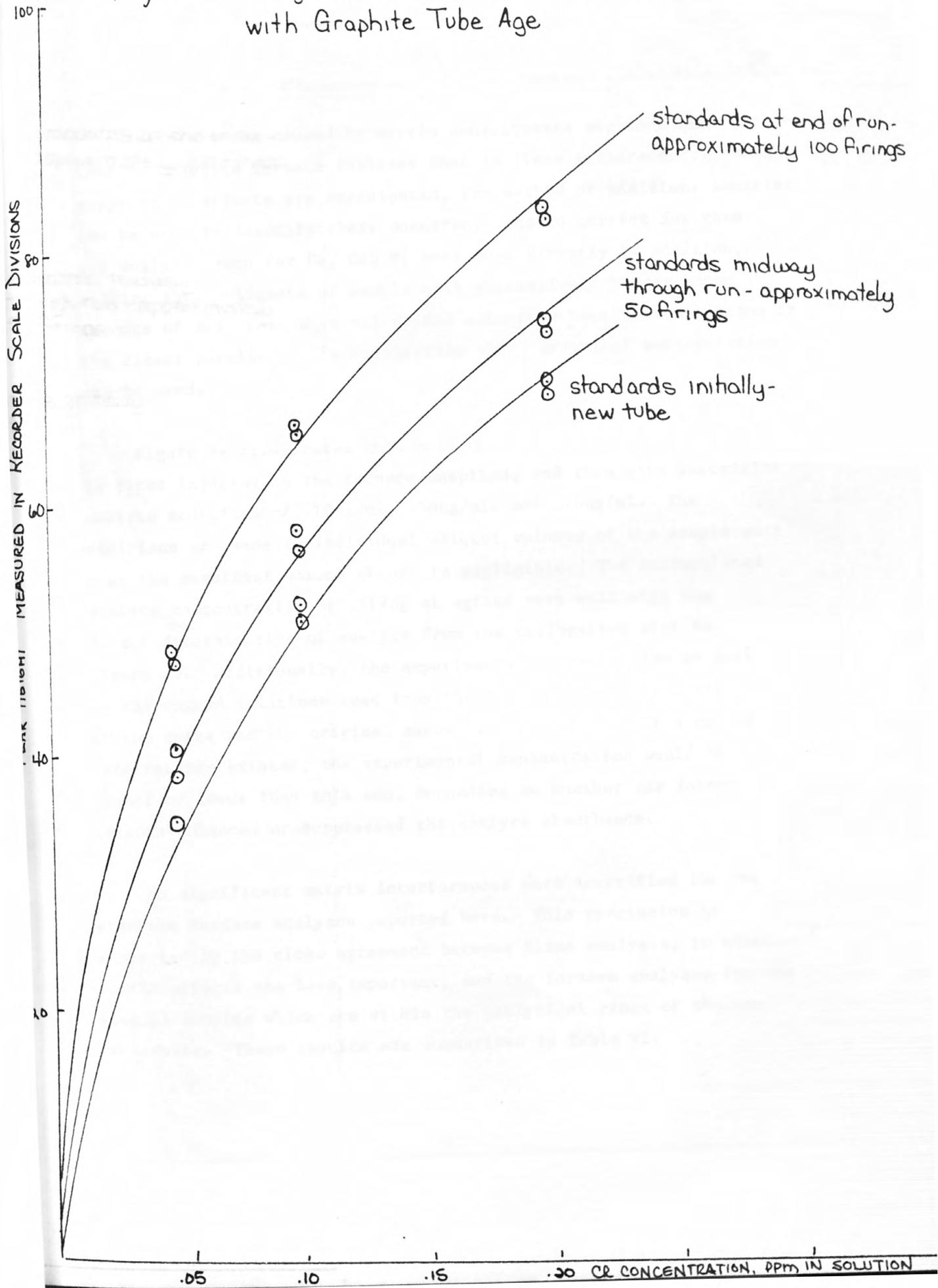
Atomic absorption is not the method of choice for low levels of Ba. Extensive interferences are found which are similar to those for Ca and Sr. Sensitivity at least in air-acetylene is very poor, on the order of 10 ug/ml for 1% absorption. In the hotter nitrous oxide-acetylene flame, Ba ionization reaches approximately 90% (Slavin, 1968). Large amounts of excess alkali are required in both sample and standard to suppress the ionization. The lowest level for accurate quantitation at best is 10 ug/ml in solution or 100 ppm in the rock samples and 500 ppm in the sulfide ores. While atomic absorption is widely used for Sr, especially in biological samples, many interferences have been reported. Control of them with La is recommended, as is ionization suppression with excess alkali (Slavin, 1968; Angino and Billings, 1967). Accuracy of Sr analyses for the standard reference materials was very poor, showing analyte recoveries on the order of 70%. The analyses are therefore not reported.

#### Graphite Furnace-Atomic Absorption Measurements:

The Perkin-Elmer AS 50 Autosampler was used exclusively for the injection of 20 ul aliquots of sample into the graphite furnace for automatically programmed atomization as detailed previously in Table Ib. Graphite tube life was approximately 150 firings. This limited the typical run to duplicate injections of the 60 solutions which could be contained in two autosampler racks. About 30% of these solutions were the 5-6 calibration standards, run as a group at the start of an analysis and repeated in random pairs after every 8-10 unknowns. Such repetition allowed correction of the original analytical curve for changes in sensitivity with graphite tube age. These changes vary from element to element and from tube to tube. They are attributable to physico-chemical changes in the graphite with repeated firing, as the analytical solution reacts with the carbon. These changes can result in variable electrical resistance of the graphite and thus produce changes in the actual atomization temperature as the tube is repeatedly used. Figure 1 illustrates the needed correction of the analytical curve over the life of the tube.

Figure 1. Changes in Cr Calibration Curve  
with Graphite Tube Age

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Interferences caused by matrix constituents are much more prevalent in graphite furnace analyses than in flame measurements. When suppression effects are anticipated, the method of additions sometimes can be used to identify their occurrence and to correct for them. A few analyses each for Co, Cr, Ni were done directly by addition, spiking three aliquots of sample with successively larger known amounts of analyte. When all spiked solutions have concentrations in the linear portion of the calibration plot, graphical extrapolation can be used.

Figure 2a illustrates this method for a sample solution which is first injected in the furnace unspiked, and then with successive analyte additions of .10ng/ml, .50ng/ml, and .70ng/ml. The additions are made to individual aliquot volumes of the sample such that the resultant volume change is negligible. The extrapolated analyte concentration of .019ng/ml agrees very well with the direct determination of analyte from the calibration plot in Figure 2b. Additionally, the experimental concentration of each of the spiked solutions read from the calibration plot is the sum of the spike and the original sample concentration. If a matrix interference existed, the experimental concentration would be higher or lower than this sum, depending on whether the interference enhanced or suppressed the analyte absorbance.

No significant matrix interferences were identified for the graphite furnace analyses reported here. This conclusion is supported by the close agreement between flame analyses, in which matrix effects are less important, and the furnace analyses for the several samples which are within the analytical range of the two procedures. These results are summarized in Table VI.

Figure 2a. Method of Additions: Graphical Extrapolation

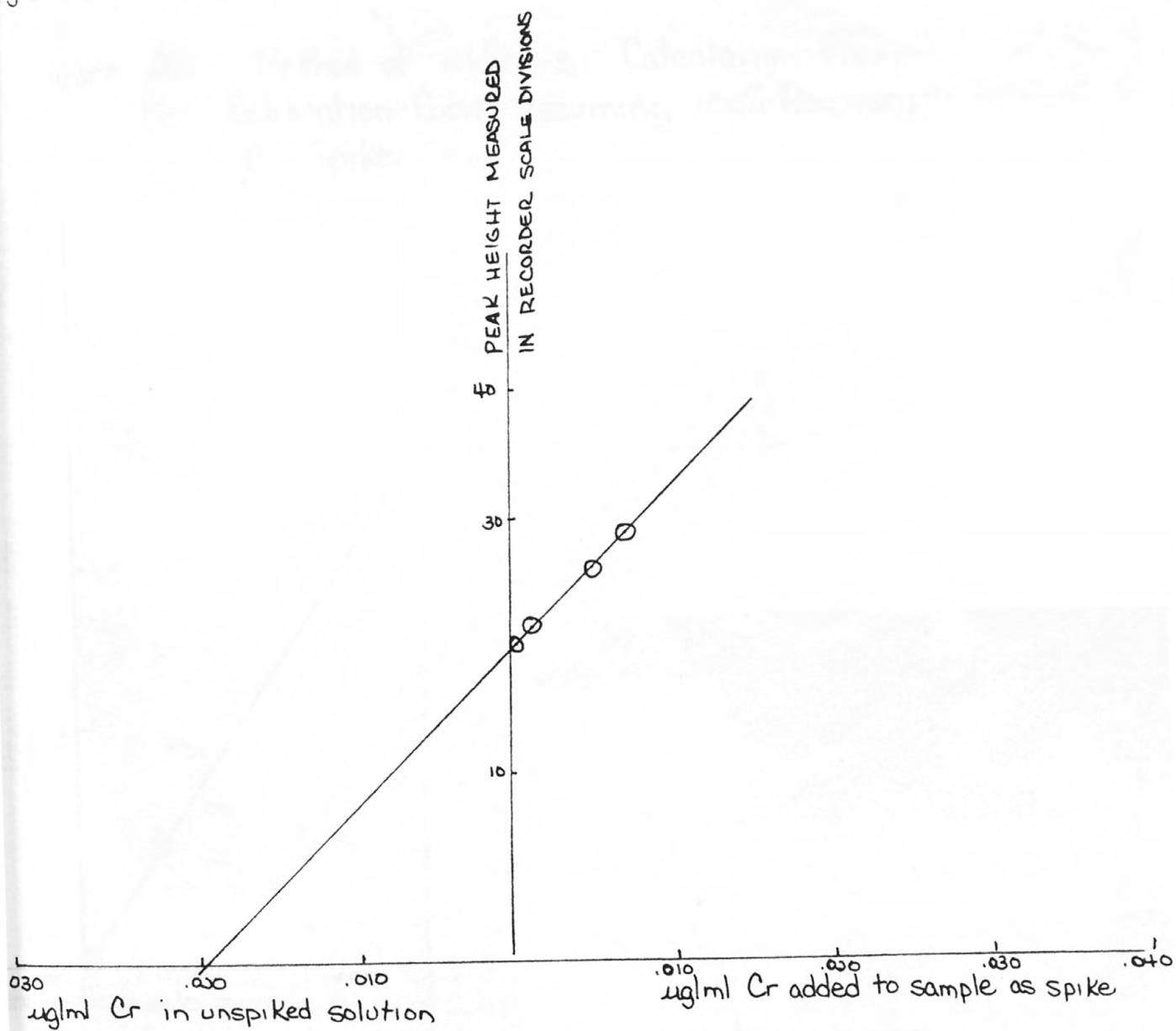
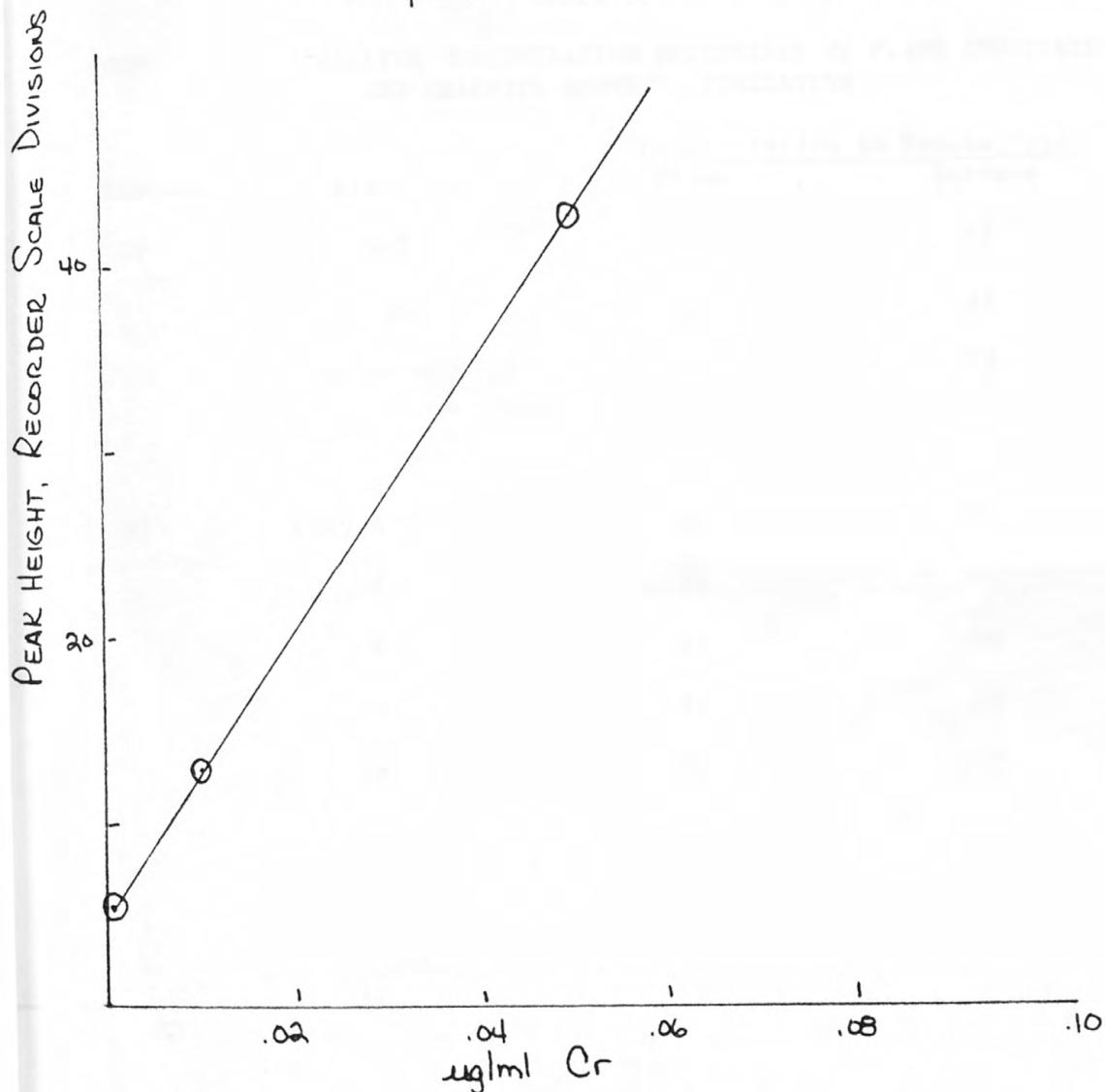


Figure 2b. Method of Additions: Calculation from Calibration Curve Assuming 100% Recovery of Spike



Sample alone	peak height	concentration .019ug/ml from calibration curve	calculated concentration sample + spike	
add .001ug/ml Cr	19	.019	.020	.020
add .005ug/ml Cr	24	.023	.023	.024
add .007ug/ml Cr	29	.026	.026	.026

calculated and experimental concentrations  
agree within error limit of method

Table VI

COMPARISON OF ANALYTE CONCENTRATION DETERMINED BY FLAME ATOMIZATION  
AND GRAPHITE FURNACE ATOMIZATION

Element	Sample	Concentration in Sample, ppm	
		Flame	Furnace
Cr	USGS G-2	13	14
	Phosphate 1	47	49
	Phosphate 2	67	72
Ni	Clay 6	25	21
	7	25	21
	8	22	16
	9	28	29
	10	38	>35

1 The analysis of standard reference materials also serves to  
2 identify analytical error resulting from interference effects,  
3 changes in the graphite tube, or other causes. In many cases,  
4 the recommended value of any analyte is the average of several  
5 "round robin" analyses which show variations far greater than  
6 the uncertainties reported for individual analyses. Agreement of  
7 10% with literature is therefore acceptable. A comparison of  
8 standard reference material analyses carried out during the  
9 course of this work and selected literature values appears in  
10 Table VII. The comparison supports the overall accuracy of these  
11 analyses. Additionally, precision is reported for all standard  
12 reference material analyses. Precision of analysis varies with  
13 analyte concentration, being poorest at low levels approaching  
14 the detection limit and at high levels where curvature of the  
15 calibration plot reduces sensitivity.

16 Complete analytical data determined by rapid rock and atomic  
17 absorption methods appear in Tables VIII, IX and X. Correlation  
18 plots comparing atomic absorption and SQS analyses (the latter  
19 reported by Harris and others (1981)) follow the tables.

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Table VII  
Results for Analyses of USGS Standard Rocks

Element	Standard Rock	Literature Values			Concentration, ppm	
		Ref 1,2	Ref 3-AAS	Ref 4-ICP	Flame Atomization	Furnace Atomization
Cu	AGV-1	avg 59.7	62±3(5)	40	53±5(3)	
	GSP-1	avg 33.3	31±4(5)		33(1)	
	G-2	avg 11.7	9±2(5)		12±.5(5)	
	QLO-1	avg 30.0			28±.1(3)	
	MnNoduleA-1	1100			1130±60(4)	
	MnNodule P-1	11,600			11,600±100(4)	
Zn	G-2	rec 85	84±2(5)		83(1)	
	QLO-1	rec 63			57±2(3)	
	MnNoduleA-1	587			598±10(4)	
	MnNoduleP-1	1595			1560±60(4)	
Ni	GSP-1	avg 9	7±1(5)	17	13(1)	7.8±3(4)
	MAG-1	avg 54	56±3(5)		50(1)	
	G-2	avg 6	<2			3.2±.4(6)
	AGV-1	avg 17	14±2			14±1(3)
	QLO-1	avg 7			3.6±2(3)	
Co	AGV-1	avg 14				18±5(4)
	G-2	avg 6				5.4±.4(6)
	GSP-1	avg 7				8.1±1(4)
	QLO-1	avg 7				8.1±1(7)

Table VII (continued)

## Results for Analyses of USGS Standard Rocks

Element	Standard Rock	Concentration, ppm			
		Ref 1,2	Literature Values	Ref 4-ICP	This Work
Cr	G-2	avg 8	6±2	16	12±5(4)
	GSP-1	avg 12	11±2		14±5(3)
	QLO-1	avg 4			2.1 (2)
	NBS 1633	cert 131			155
	NBS 1633a	cert 196			206
V	AGV-1	avg 125	120±8		110±17(6)
	G-2	avg 36	33±4		46±15(4)
	GSP-1	avg 54	51±5	60	58±18 6
Ba	G-2	rec 1870	2150±180		1900
	BCR-1	rec 675	743±78	661	765
	QLO-1	avg 1300			1450

One figure more than the two significant figures is sometimes shown in this table for comparison only. Literature values probably show more figures than are significant where three or more are shown.

<sup>1</sup> Flanagan, F.J., USGS Professional Paper 840, pp. 171-172 and Flanagan, F.J. and Gottfried, David, USGS Professional Paper 1155, pp. 36 39.

<sup>2</sup> Reported values are qualified as recommended, average, or range.

<sup>2</sup> NBS, 1974 Certificate of Analysis

<sup>3</sup> NBS, 1979 Certificate of Analysis

<sup>4</sup> Bothner, M.H. et al., Estuarine and Coastal Marine Science, 10.

<sup>4</sup> Floyd, M.A. et al., Anal. Chem. 52 2166-2173, 1980.

Table VIII

## RAPID ROCK ANALYSIS

## MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Syenite					
	S1	S2	S3	S4	S5	S6
SiO <sub>2</sub>	62.1	61.0	63.2	61.2	61.3	64.3
Al <sub>2</sub> O <sub>3</sub>	14.7	16.7	14.8	16.9	17.6	17.0
Fe <sub>2</sub> O <sub>3</sub>	4.2	2.0	6.5	3.5	2.9	2.2
FeO	2.2	3.4	1.3	2.5	1.8	1.3
MgO	0.60	0.48	0.34	0.34	0.44	0.27
CaO	1.2	1.6	0.66	1.1	1.1	0.69
Na <sub>2</sub> O	7.1	7.0	6.8	7.4	6.6	6.7
K <sub>2</sub> O	5.3	4.8	5.2	5.7	5.6	5.6
H <sub>2</sub> O <sup>+</sup>	0.64	0.77	0.91	0.92	1.1	0.70
H <sub>2</sub> O <sup>-</sup>	0.16	0.06	0.04	0.08	0.42	0.20
TiO <sub>2</sub>	0.50	0.56	0.44	0.40	0.40	0.30
P <sub>2</sub> O <sub>5</sub>	0.13	0.19	0.08	0.12	0.10	0.10
MnO	0.37	0.21	0.27	0.22	0.16	0.16
CO <sub>2</sub>	0.06	0.08	0.10	0.04	0.32	0.20
Total	99	99	101	100	100	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	6.6	5.7	7.9	6.3	4.9	3.6

Table VIII

## RAPID ROCK ANALYSIS

## MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Syenite					
	S7	S8	S9	S10	S11	S12
SiO <sub>2</sub>	63.4	62.1	60.8	60.2	62.3	61.7
Al <sub>2</sub> O <sub>3</sub>	17.2	17.5	17.5	15.0	16.6	17.6
Fe <sub>2</sub> O <sub>3</sub>	2.1	2.1	3.3	5.4	2.4	3.0
FeO	2.0	2.4	1.4	1.7	2.4	2.2
MgO	0.13	0.45	0.55	0.22	0.38	0.28
CaO	0.63	1.1	1.5	2.1	1.2	0.95
Na <sub>2</sub> O	7.4	6.7	6.7	7.0	6.9	7.8
K <sub>2</sub> O	5.7	6.1	4.7	4.9	5.4	5.3
H <sub>2</sub> O <sup>+</sup>	0.64	0.80	1.1	0.58	0.63	0.77
H <sub>2</sub> O <sup>-</sup>	0.08	0.16	0.38	0.26	0.28	0.08
TiO <sub>2</sub>	0.23	0.51	0.57	0.42	0.48	0.34
P <sub>2</sub> O <sub>5</sub>	0.07	0.13	0.19	0.06	0.12	0.10
MnO	0.16	0.14	0.11	0.28	0.17	0.17
CO <sub>2</sub>	0.06	0.04	0.82	1.2	0.32	0.06
Total	100	100	100	99	99	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	4.3	4.6	4.8	7.3	6.0	5.3

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Syenite					
	S13	S14	S15	S16	S17	S18
SiO <sub>2</sub>	56.7	60.7	60.2	61.5	59.9	61.4
Al <sub>2</sub> O <sub>3</sub>	17.6	17.7	17.5	17.5	17.6	16.6
Fe <sub>2</sub> O <sub>3</sub>	2.7	3.5	2.7	3.0	1.8	4.4
FeO	4.2	1.7	2.9	2.3	3.2	1.0
MgO	1.5	0.22	0.31	0.27	0.76	0.31
CaO	3.4	0.91	1.5	1.2	2.0	1.5
Na <sub>2</sub> O	6.3	8.1	6.8	7.3	6.7	6.9
K <sub>2</sub> O	3.8	5.3	5.3	5.2	4.6	4.6
H <sub>2</sub> O+	1.0	0.74	0.90	0.68	1.1	0.86
H <sub>2</sub> O-	0.36	0.26	0.44	0.26	0.04	0.28
TiO <sub>2</sub>	1.1	0.26	0.58	0.37	0.62	0.54
P <sub>2</sub> O <sub>5</sub>	0.44	0.09	0.15	0.11	0.22	0.14
MnO	0.18	0.16	0.17	0.16	0.14	0.24
CO <sub>2</sub>	0.94	0.06	0.09	0.18	0.73	0.91
Total	100	100	100	100	99	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	7.3	5.4	5.9	5.4	5.3	5.5

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Syenite					
	S19	S20	S21	S22	S23	S24
SiO <sub>2</sub>	63.6	66.2	62.5	62.7	62.6	62.4
Al <sub>2</sub> O <sub>3</sub>	15.5	14.5	16.6	15.0	15.9	17.1
Fe <sub>2</sub> O <sub>3</sub>	6.9	5.4	3.4	4.5	4.1	2.6
FeO	0.76	0.76	1.6	2.1	1.6	2.4
MgO	0.11	0.09	0.40	0.35	0.24	0.48
CaO	0.22	0.37	1.1	1.1	0.99	1.3
Na <sub>2</sub> O	5.7	5.7	6.9	7.2	7.2	6.9
K <sub>2</sub> O	5.2	4.5	5.7	4.9	5.2	5.1
H <sub>2</sub> O+	0.82	1.2	0.21	0.38	0.44	0.69
H <sub>2</sub> O-	0.38	0.44	0.30	0.38	0.46	0.36
TiO <sub>2</sub>	0.54	0.28	0.36	0.42	0.43	0.54
P <sub>2</sub> O <sub>5</sub>	0.10	0.08	0.11	0.14	0.08	0.21
MnO	0.18	0.22	0.16	0.35	0.21	0.17
CO <sub>2</sub>	0.02	0.17	0.49	0.07	0.25	0.02
Total	100	100	100	100	100	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	7.7	6.2	5.2	6.8	5.8	5.2

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Syenite					
	S25	S26	S27	S28	S29	S30
SiO <sub>2</sub>	63.0	63.4	60.9	63.4	62.4	61.2
Al <sub>2</sub> O <sub>3</sub>	16.5	18.1	15.6	13.7	14.6	16.2
Fe <sub>2</sub> O <sub>3</sub>	4.0	3.1	5.2	6.7	2.5	2.4
FeO	1.0	0.72	1.9	1.9	5.8	4.7
MgO	0.43	0.27	0.29	0.28	0.30	0.35
CaO	0.85	0.74	1.8	1.0	0.78	1.2
Na <sub>2</sub> O	6.0	6.9	7.0	5.2	6.7	7.5
K <sub>2</sub> O	5.6	5.0	4.7	4.6	4.6	4.5
H <sub>2</sub> O+	0.96	0.76	0.60	1.2	0.54	0.62
H <sub>2</sub> O-	0.50	0.38	0.40	0.61	0.28	0.30
TiO <sub>2</sub>	0.48	0.54	0.40	0.46	0.52	0.42
P <sub>2</sub> O <sub>5</sub>	0.16	0.20	0.15	0.11	0.12	0.15
MnO	0.17	0.09	0.16	0.28	0.26	0.19
CO <sub>2</sub>	0.28	0.06	0.76	0.56	0.25	0.62
Total	100	100	100	100	100	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	5.1	3.9	7.3	8.8	8.9	7.6

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Syenite					
	S31	S32	S33	S34	S35	S36
SiO <sub>2</sub>	62.8	63.9	64.9	65.2	65.2	60.7
Al <sub>2</sub> O <sub>3</sub>	15.7	15.4	15.7	15.8	14.4	16.7
Fe <sub>2</sub> O <sub>3</sub>	7.0	4.9	4.3	4.7	5.5	3.8
FeO	0.38	1.0	0.76	0.72	0.82	1.6
MgO	0.21	0.15	0.12	0.14	0.12	0.39
CaO	0.55	0.92	0.74	0.33	0.56	1.9
Na <sub>2</sub> O	6.4	6.2	5.8	5.5	5.5	6.5
K <sub>2</sub> O	4.1	4.9	5.1	5.3	4.9	4.4
H <sub>2</sub> O+	1.1	0.81	0.90	1.5	1.2	1.2
H <sub>2</sub> O-	0.78	0.36	0.62	0.26	0.34	0.38
TiO <sub>2</sub>	0.50	0.40	0.32	0.28	0.26	0.49
P <sub>2</sub> O <sub>5</sub>	0.14	0.11	0.09	0.08	0.07	0.15
MnO	0.22	0.12	0.12	0.12	0.14	0.17
CO <sub>2</sub>	0.12	0.47	0.06	0.03	0.03	1.2
Total	100	100	100	100	99	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	7.4	6.0	5.1	5.5	6.4	5.4

Table VIII

## RAPID ROCK ANALYSIS

## MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Syenite					
	S37	S38	S39	S40	S41	S42
SiO <sub>2</sub>	66.7	62.7	69.1	65.3	62.8	62.4
Al <sub>2</sub> O <sub>3</sub>	18.1	15.8	14.3	16.6	16.3	16.6
Fe <sub>2</sub> O <sub>3</sub>	0.61	1.4	3.7	2.5	4.6	2.6
FeO	0.56	4.1	1.4	1.2	1.3	3.0
MgO	0.07	0.45	0.12	0.20	0.14	0.35
CaO	0.27	0.98	0.25	0.28	0.33	1.5
Na <sub>2</sub> O	6.8	6.6	5.6	6.5	6.6	6.7
K <sub>2</sub> O	5.6	4.8	4.6	5.4	5.1	4.7
H <sub>2</sub> O+	0.54	0.76	0.52	0.92	0.92	0.82
H <sub>2</sub> O-	0.26	0.10	0.24	0.28	0.42	0.48
TiO <sub>2</sub>	0.17	0.28	0.22	0.18	0.46	0.52
P <sub>2</sub> O <sub>5</sub>	0.07	0.07	0.05	0.07	0.11	0.16
MnO	0.03	0.18	0.07	0.09	0.27	0.17
CO <sub>2</sub>	0.03	1.9	0.04	0.14	0.12	0.38
Total	100	100	100	100	99	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	1.2	5.9	5.2	3.8	6.0	5.9

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Syenite					
	S43	S44	S45	S46	S47	S48
SiO <sub>2</sub>	69.7	63.8	64.0	57.1	64.0	60.1
Al <sub>2</sub> O <sub>3</sub>	13.0	15.5	15.6	14.7	15.3	15.5
Fe <sub>2</sub> O <sub>3</sub>	4.1	3.4	4.0	8.1	3.0	5.8
FeO	1.3	2.5	2.3	0.44	3.2	1.8
MgO	0.08	0.19	0.18	0.27	0.17	0.54
CaO	0.45	0.96	0.72	3.4	0.82	2.2
Na <sub>2</sub> O	5.6	6.5	7.0	5.8	6.4	6.4
K <sub>2</sub> O	4.7	5.2	5.0	3.8	5.2	3.7
H <sub>2</sub> O <sup>+</sup>	0.61	0.92	0.66	1.3	0.50	1.1
H <sub>2</sub> O <sup>-</sup>	0.22	0.22	0.34	0.70	0.46	0.30
TiO <sub>2</sub>	0.24	0.36	0.56	0.96	0.38	0.74
P <sub>2</sub> O <sub>5</sub>	0.06	0.10	0.14	0.51	0.10	0.21
MnO	0.16	0.23	0.13	0.27	0.27	0.21
CO <sub>2</sub>	0.04	0.46	0.04	1.9	0.17	1.4
Total	100	100	101	99	100	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	5.5	6.2	6.5	8.6	6.5	7.8

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Syenite					
	S49	S50	S51	S52	S53	S54
SiO <sub>2</sub>	60.8	64.5	65.2	68.3	66.1	62.2
Al <sub>2</sub> O <sub>3</sub>	15.8	16.4	15.5	14.8	15.3	15.6
Fe <sub>2</sub> O <sub>3</sub>	4.3	3.9	2.2	1.6	2.2	1.8
FeO	2.0	2.0	2.2	2.5	2.5	4.4
MgO	0.20	0.12	0.17	0.10	0.16	0.74
CaO	1.5	0.72	1.2	0.72	1.3	2.1
Na <sub>2</sub> O	6.2	6.3	6.0	5.9	6.2	6.5
K <sub>2</sub> O	5.0	5.4	5.2	5.0	5.2	4.2
H <sub>2</sub> O <sup>+</sup>	1.1	0.78	0.82	0.63	0.42	0.78
H <sub>2</sub> O <sup>-</sup>	0.40	0.46	0.28	0.18	0.42	0.32
TiO <sub>2</sub>	0.34	0.34	0.36	0.28	0.38	0.70
P <sub>2</sub> O <sub>5</sub>	0.11	0.11	0.08	0.08	0.09	0.29
MnO	0.22	0.10	0.20	0.15	0.22	0.21
CO <sub>2</sub>	1.1	0.14	0.36	0.03	0.42	0.44
Total	99	101	100	100	101	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	6.5	6.1	4.6	4.3	4.9	6.6

Table VIII

## RAPID ROCK ANALYSIS

## MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Syenite					
	S55	S56	S57	S58	S59	S60
SiO <sub>2</sub>	63.1	67.1	71.1	63.8	66.4	65.1
Al <sub>2</sub> O <sub>3</sub>	15.2	15.1	14.2	15.3	15.5	15.3
Fe <sub>2</sub> O <sub>3</sub>	2.3	1.9	1.5	1.6	1.8	3.7
FeO	3.9	2.8	2.0	4.2	3.2	0.84
MgO	0.58	0.17	0.08	0.59	0.20	0.18
CaO	1.6	0.87	0.46	1.7	1.4	1.4
Na <sub>2</sub> O	6.3	5.9	5.6	6.4	6.3	5.6
K <sub>2</sub> O	4.3	5.1	4.8	4.4	4.6	5.1
H <sub>2</sub> O <sup>+</sup>	1.0	0.63	0.57	0.80	0.70	1.1
H <sub>2</sub> O <sup>-</sup>	0.06	0.22	0.06	0.04	0.30	0.32
TiO <sub>2</sub>	0.65	0.32	0.25	0.63	0.36	0.36
P <sub>2</sub> O <sub>5</sub>	0.26	0.08	0.07	0.24	0.11	0.07
MnO	0.22	0.14	0.09	0.18	0.15	0.21
CO <sub>2</sub>	0.27	0.05	0.07	0.19	0.29	0.79
Total	100	100	101	100	101	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	6.6	5.0	3.7	6.2	5.3	4.6

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Syenite					
	S61	S62	S63	S64	S65	S66
SiO <sub>2</sub>	62.8	63.0	63.5	63.3	64.1	65.2
Al <sub>2</sub> O <sub>3</sub>	16.2	15.2	16.0	15.6	15.8	16.0
Fe <sub>2</sub> O <sub>3</sub>	1.7	2.1	1.7	1.9	2.3	2.0
FeO	3.6	3.9	3.9	3.8	3.4	2.5
MgO	0.58	0.54	0.52	0.57	0.59	0.18
CaO	1.7	1.8	1.6	1.7	1.3	1.1
Na <sub>2</sub> O	6.4	6.5	6.4	6.5	6.3	6.2
K <sub>2</sub> O	4.5	4.4	4.6	4.4	4.3	5.2
H <sub>2</sub> O <sup>+</sup>	0.64	0.69	0.42	0.70	0.80	0.64
H <sub>2</sub> O <sup>-</sup>	0.24	0.22	0.44	0.30	0.30	0.20
TiO <sub>2</sub>	0.62	0.62	0.56	0.61	0.61	0.32
P <sub>2</sub> O <sub>5</sub>	0.22	0.25	0.21	0.22	0.24	0.10
MnO	0.20	0.20	0.20	0.21	0.16	0.17
CO <sub>2</sub>	0.39	0.42	0.20	0.28	0.02	0.47
Total	100	100	100	100	100	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	5.7	6.4	5.9	6.1	6.0	4.7

Table VIII

## RAPID ROCK ANALYSIS

## MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Greywacke					
	M1	M2	M3	M4	M5	M6
SiO <sub>2</sub>	66.9	70.1	67.2	63.1	65.9	66.1
Al <sub>2</sub> O <sub>3</sub>	13.4	12.9	13.5	13.4	13.8	13.4
Fe <sub>2</sub> O <sub>3</sub>	3.7	3.0	3.5	5.3	4.2	4.1
FeO	1.6	1.9	2.3	2.8	2.5	2.3
MgO	2.9	2.4	2.8	3.5	3.0	2.7
CaO	2.5	2.0	2.2	3.1	2.6	2.3
Na <sub>2</sub> O	1.9	2.8	2.9	2.6	3.0	2.9
K <sub>2</sub> O	2.7	2.0	2.2	1.6	2.1	2.1
H <sub>2</sub> O <sup>+</sup>	1.9	2.1	1.9	2.5	2.0	2.0
H <sub>2</sub> O <sup>-</sup>	0.46	<.01	0.66	0.28	0.24	0.30
TiO <sub>2</sub>	0.74	0.60	0.73	1.4	0.89	0.84
P <sub>2</sub> O <sub>5</sub>	0.17	0.16	0.20	0.29	0.24	0.21
MnO	0.12	0.11	0.14	0.15	0.16	0.16
CO <sub>2</sub>	0.84	0.31	0.57	0.10	0.13	0.44
Total	100	100	101	100	101	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	5.5	5.1	6.0	8.4	6.9	6.6

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Greywacke					
	M7	M8	M9	M10	M11	M12
SiO <sub>2</sub>	67.0	67.2	67.7	63.4	68.3	68.4
Al <sub>2</sub> O <sub>3</sub>	13.6	12.7	13.2	13.1	11.6	12.6
Fe <sub>2</sub> O <sub>3</sub>	4.0	3.2	3.1	4.2	3.3	3.6
FeO	2.4	2.6	2.8	3.1	1.9	1.6
MgO	3.1	3.8	2.9	4.0	2.6	2.3
CaO	2.6	2.9	2.1	3.0	3.8	2.6
Na <sub>2</sub> O	2.9	3.0	2.7	2.6	2.7	2.2
K <sub>2</sub> O	1.6	0.98	1.9	1.8	1.4	2.3
H <sub>2</sub> O <sup>+</sup>	1.8	2.3	2.2	2.4	1.9	2.0
H <sub>2</sub> O <sup>-</sup>	0.48	0.24	0.08	0.16	0.08	0.20
TiO <sub>2</sub>	0.72	0.65	0.76	1.0	0.72	0.68
P <sub>2</sub> O <sub>5</sub>	0.20	0.16	0.21	0.21	0.17	0.18
MnO	0.18	0.15	0.11	0.18	0.12	0.12
CO <sub>2</sub>	0.04	0.58	0.35	1.1	1.7	1.8
Total	101	100	100	100	100	101
Fe as Fe <sub>2</sub> O <sub>3</sub>	6.6	6.1	6.2	7.6	5.4	5.4

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Greywacke					Siltstone
	M13	M14	M15	M16	M17	M18
SiO <sub>2</sub>	65.8	65.4	68.9	59.4	61.8	60.3
Al <sub>2</sub> O <sub>3</sub>	13.5	13.7	13.0	14.2	15.5	15.7
Fe <sub>2</sub> O <sub>3</sub>	2.3	4.0	3.3	2.1	4.2	2.3
FeO	3.7	2.3	2.1	4.0	2.8	4.6
MgO	3.3	3.0	2.5	5.8	4.3	3.8
CaO	3.9	2.6	2.6	3.0	1.7	3.1
Na <sub>2</sub> O	3.0	2.8	2.5	3.0	2.4	2.4
K <sub>2</sub> O	0.98	1.7	1.6	1.2	3.1	2.6
H <sub>2</sub> O <sup>+</sup>	2.4	2.3	2.1	3.9	2.8	3.5
H <sub>2</sub> O <sup>-</sup>	0.08	0.16	0.16	0.46	0.34	<.01
TiO <sub>2</sub>	0.83	0.81	0.74	0.71	0.89	0.81
P <sub>2</sub> O <sub>5</sub>	0.23	0.80	0.20	0.18	0.28	0.25
MnO	0.15	0.12	0.12	0.12	0.11	0.13
CO <sub>2</sub>	0.02	0.37	0.37	2.1	0.23	1.3
Total	100	100	100	100	100	101
Fe as Fe <sub>2</sub> O <sub>3</sub>	6.4	6.3	5.6	6.4	7.3	7.4

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Siltstone					
	M19	M20	M21	M22	M23	M24
SiO <sub>2</sub>	63.6	59.4	62.0	59.6	59.3	51.3
Al <sub>2</sub> O <sub>3</sub>	14.9	16.4	15.7	16.4	15.7	11.9
Fe <sub>2</sub> O <sub>3</sub>	2.5	5.5	4.7	5.5	5.0	1.5
FeO	4.0	2.6	2.2	2.1	2.4	4.2
MgO	3.5	4.2	3.9	4.0	4.2	3.5
CaO	2.4	3.3	2.0	2.8	2.3	11.7
Na <sub>2</sub> O	2.8	2.4	2.0	1.5	1.4	2.3
K <sub>2</sub> O	1.9	2.4	3.2	3.7	3.7	1.1
H <sub>2</sub> O <sup>+</sup>	3.0	2.3	3.1	2.9	3.2	2.8
H <sub>2</sub> O <sup>-</sup>	0.16	0.34	0.12	0.12	0.26	0.24
TiO <sub>2</sub>	0.87	0.96	0.88	0.88	0.82	0.68
P <sub>2</sub> O <sub>5</sub>	0.24	0.28	0.26	0.30	0.27	0.24
MnO	0.11	0.16	0.12	0.12	0.12	0.18
CO <sub>2</sub>	0.49	0.20	0.21	0.30	1.1	8.8
Total	100	100	100	100	100	100
Fe as Fe <sub>2</sub> O <sub>3</sub>	6.9	8.4	7.1	7.8	7.6	6.1

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

	Sample Identification: Siltstone				
	M25	M26	M27	M28	M29
SiO <sub>2</sub>	63.1	62.3	51.6	64.6	64.1
Al <sub>2</sub> O <sub>3</sub>	15.1	15.9	11.3	14.3	13.8
Fe <sub>2</sub> O <sub>3</sub>	3.5	2.0	1.6	1.9	1.3
FeO	3.3	5.1	3.7	4.4	5.0
MgO	3.8	3.5	6.2	4.6	3.4
CaO	2.4	2.3	10.7	0.96	3.2
Na <sub>2</sub> O	2.6	2.3	2.8	2.9	2.4
K <sub>2</sub> O	2.0	2.2	0.42	1.4	1.7
H <sub>2</sub> O <sup>+</sup>	2.9	3.2	3.2	3.3	3.1
H <sub>2</sub> O <sup>-</sup>	0.24	0.32	0.34	0.44	0.16
TiO <sub>2</sub>	0.86	0.91	0.68	0.71	0.88
P <sub>2</sub> O <sub>5</sub>	0.27	0.29	0.18	0.17	0.30
MnO	0.12	0.13	0.17	0.07	0.12
CO <sub>2</sub>	0.42	0.22	8.1	0.18	1.8
Total	101	101	101	100	101
Fe as Fe <sub>2</sub> O <sub>3</sub>	7.1	7.6	5.7	6.7	6.8

Table VIII  
RAPID ROCK ANALYSIS  
MAJOR ELEMENTS CONCENTRATION IN PERCENT

Sample Identification	Phosphate		
	A	B	C
SiO <sub>2</sub>	9.8	16.2	4.8
Al <sub>2</sub> O <sub>3</sub>	3.2	0.78	1.3
Fe <sub>2</sub> O <sub>3</sub>	16.4	2.4	3.5
FeO	-----	-----	-----
MgO	0.64	0.36	3.4
CaO	31.0	44.9	45.2
Na <sub>2</sub> O	0.58	0.33	0.64
K <sub>2</sub> O	0.24	0.04	0.07
H <sub>2</sub> O <sup>+</sup>	3.7	1.3	1.9
H <sub>2</sub> O <sup>-</sup>	2.6	0.86	1.6
TiO <sub>2</sub>	0.11	0.04	0.06
P <sub>2</sub> O <sub>5</sub>	19.7	21.5	24.8
MnO	0.09	0.16	0.23
CO <sub>2</sub>	1.8	10.5	9.7
S	13.3	1.8	2.8
Total	-----	101	100

\* The iron in phosphate sample A is reported as total iron as Fe<sub>2</sub>O<sub>3</sub>. The high summation for this sample may be due to the presence of FeS<sub>2</sub> (pyrite).

\* The iron in samples B and C are reported as total iron as Fe<sub>2</sub>O<sub>3</sub>.

Table VIIa  
Rapid Rock Analysis

Total Sulfur Concentration in percent

<u>Sample Identification</u>	<u>Percent Total Sulfur</u>
------------------------------	-----------------------------

Darahib Sulfide

1	8.0
2	26.4
3	26.7
4	17.4
5	15.0

Umm Samiuki,  
eastern  
emine Sulfide

1	12.6
2	14.4
3	21.4
4	11.3
5	3.1
6	3.0
7	5.1

Hamata Sulfide

1	13.9
2	7.6

Maakal Sulfide

1	3.3
---	-----

## RESULTS

Table IX  
FLAME ATOMIC ABSORPTION ANALYSES

## C O N C E N T R A T I O N S

Sample Identification	Cu ppm	Zn ppm	Ni ppm	Cr ppm	Ba ppm
Syenite S1	10	140	-	-	-
S2	18	100	-	-	-
S11	9.9	100	-	-	-
S12	9.2	130	-	-	-
S29	41	200	-	31	-
S31	8.6	66	-	6.7	-
S33	10	140	-	-	-
S51	12	170	-	-	-
S52	12	180	-	8.8	-
S55	17	230	-	9.4	-
Greywacke M1	23	59	42	90	-
M2	34	53	39	75	-
M3	46	67	50	97	-
M4	50	93	46	260	-
M5	38	72	42	140	-
M16	40	76	170	260	-
Siltstone M17	43	100	48	140	-
M18	61	98	56	110	-
M19	51	80	62	140	-
M20	39	100	80	150	-

Table IX

## FLAME ATOMIC ABSORPTION ANALYSES

## C O N C E N T R A T I O N S

Sample Identification	Cu ppm	Zn ppm	Ni ppm	Cr ppm	Ba ppm
Gypsum G1	7.7	98	--	--	<50
G2	10	110	--	--	57
G3	11	78	--	--	<50
G4	6.6	66	--	--	<50
G5	7.7	22	--	--	<50
G6	5.2	58	--	--	<50
G7	14	54	--	--	50
G8	4.6	170	--	--	<50
G9	4.0	56	--	--	<50
G10	2.9	35	--	--	<50
Lime Grit-LG1	7.6	3200	43	--	220
LG2	6.9	1400	12	--	51
LG3	9.6	4000	26	--	160
LG4	13	920	28	--	210
LG5	4.7	1500	12	--	190
LG6	10	1700	23	--	110
LG7	11	1300	36	--	86
LG8	7.0	1000	43	--	64
LG9	7.5	2600	9.8	--	75
LG10	6.3	1300	11	--	74

Table IX  
FLAME ATOMIC ABSORPTION ANALYSES

C O N C E N T R A T I O N S					
Sample Identification	Cu ppm	Zn ppm	Ni ppm	Cr ppm	Ba ppm
Lime Grit					
LG11	6.7	420	17	-	<50
LG12	4.8	290	12	-	110
Conglomerate					
C1	8.4	790	-	-	90
C2	13	900	-	-	90
C3	9.3	1500	-	-	320
C4	12	730	-	-	110
C5	9.1	740	-	-	99
C6	7.2	520	-	-	120
C7	12	1200	-	-	140
C8	56	1300	-	-	1700
C9	11	1200	-	-	100
C10	20	1500	-	-	290
Clay					
CL1	37	920	30	130	270
CL2	51	950	27	150	-
CL3	49	800	29	140	-
CL4	37	590	24	150	-
CL5	110	300	31	130	280
CL6	59	640	23	130	230
CL7	58	340	26	180	250

Table IX

## FLAME ATOMIC ABSORPTION ANALYSES

## C O N C E N T R A T I O N S

Sample Identification		Cu ppm	Zn ppm	Ni ppm	Cr ppm	Ba ppm
Clay	CL8	44	320	19	130	230
	CL9	120	550	28	140	220
	CL10	43	270	32	130	200
Oil Tainted Limestone	OL1	11	270	-	-	120
	OL2	18	390	-	-	150
	OL3	14	54	-	-	67
	OL4	6.1	91	-	-	31
	OL5	7.2	132	-	-	85
	OL6	9.8	590	-	-	50
	OL7	2.3	710	-	-	75
	OL8	4.3	380	-	-	35
	OL9	5.4	820	-	-	25
	OL10	8.4	230	-	-	45
Phosphate	A	33	33	110	45	-
	B	18	180	12	71	-
	C	17	56	22	26	170

Table IX

## FLAME ATOMIC ABSORPTION ANALYSES

C O N C E N T R A T I O N S					
Sample Identification	Cu %	Zn %	Cd ppm	Cr ppm	Ba ppm
Darahib Sulfide 1	2.5	5.1	410	-	<250
	11	20	2200	-	<250
	12	6.7	550	-	<250
	3.0	23	2300	-	<250
	9.5	8.9	690	-	<250
Umm Samiuki, eastern emine Sulfide 1	2.3	16	460	-	<250
	1.5	5.1	130	-	<250
	2.5	30	870	-	<250
	1.4	3.9	90	-	<250
	7.8	19	210	-	<250
	12	23	150	-	<250
	17	18	350	-	<250
Hamata Sulfide 1	5.5	14	1000	-	<250
	.018	.058	<75	-	<250
Maakal Sulfide 1	.0040	.013	<75	-	<250

Table IX

GRAPHITE FURNACE ATOMIC ABSORPTION ANALYSES

C O N C E N T R A T I O N S					
Sample Identification	Ni ppm	Co ppm	V ppm	Cr ppm	Cd ppm
Syenite S1	6.0	<1.0	*	7.0	1.3
	12	1.5	*	9.4	0.26
	3.5	<1.0	*	6.4	0.58
	3.0	1.1	*	5.8	0.42
	11	1.8	*	31	0.62
	3.0	<1.0	*	6.1	0.20
	7.3	1.2	*	10.	0.66
	3.4	1.0	*	6.6	1.2
	7.0	0.60	*	6.5	0.50
	37	1.3	*	8.6	0.70
Greywacke M1	-	-	-	-	0.37
	-	12	82	-	0.19
	-	17	83	-	0.25
	-	19	100	-	0.36
	-	13	60	-	0.32
	-	14	96	-	-

\*Not done, as semiquantitative spectroscopy analysis indicates all are below detection limit of 25 ppm.

Table X

## GRAPHITE FURNACE ATOMIC ABSORPTION ANALYSES

## C O N C E N T R A T I O N S

Sample Identification	Ni ppm	Co ppm	V ppm	Cr ppm	Cd ppm
Siltstone M17	-	13	110	-	-
M18	-	15	140	-	-
M19	-	13	170	-	-
Gypsum G1	5.2	1.3	<10	3.5	3.7
G2	10	1.3	<10	5.0	5.4
G3	3.3	<1.0	<10	5.5	0.62
G4	1.5	<1.0	<10	2.3	0.52
G5	1.5	<1.0	<10	1.7	<.10
G6	2.7	<1.0	<10	3.0	0.34
G7	3.6	<1.0	<10	3.0	0.73
G8	2.7	<1.0	<10	3.0	7.6
G9	<1.0	<1.0	<10	3.0	1.1
G10	1.0	<1.0	<10	1.2	0.61
Lime Grit LG1	>32	3.0	12	6.0	5.7
LG2	14	1.0	<10	4.8	1.0
LG3	>32	4.0	14	5.7	7.7
LG4	32	7.5	12	8.0	1.4
LG5	11	2.8	10	3.0	3.8

Table X

## GRAPHITE FURNACE ATOMIC ABSORPTION ANALYSES

## C O N C E N T R A T I O N S

Sample Identification	Ni ppm	Co ppm	V ppm	Cr ppm	Cd ppm
Lime Grit LG6	19	8.0	28	6.7	0.70
LG7	30	6.0	12	8.0	0.60
LG8	>32	4.2	<10	8.4	1.1
LG9	10	1.6	<10	4.7	1.3
LG10	9.2	1.2	10	4.7	0.86
LG11	15	1.4	<10	16	0.46
LG12	11	1.4	<10	12	0.31
<hr/>					
Conglomerate C1	5.9	1.4	22	22	2.9
C2	6.0	1.9	<10	15	1.5
C3	11	5.0	<10	5.7	5.2
C4	8.2	2.6	27	36	1.3
C5	14	2.3	<10	10	2.7
C6	5.7	1.7	15	3.0	0.60
C7	13	3.0	74	8.7	2.4
C8	35	9.0	60	50	1.3
C9	8.7	2.4	34	27	1.4
C10	18	4.7	50	41	1.5
<hr/>					
Clay CL1	-	5.0	93	-	0.85
CL2	-	4.0	110	-	0.09

Table X

## GRAPHITE FURNACE ATOMIC ABSORPTION ANALYSES

## C O N C E N T R A T I O N S

Sample Identification	Ni ppm	Co ppm	V ppm	Cr ppm	Cd ppm
Clay CL3	-	28	87	-	0.22
CL4	-	4.0	110	-	0.15
CL5	-	3.7	82	-	0.05
CL6	-	5.5	110	-	0.25
CL7		5.5	110	-	0.10
CL8	-	4.6	120	-	0.10
CL9	-	9.7	74	-	0.10
CL10	-	38	81	-	<.05
Oil Tainted Limestone OL1	3.7	1.0	<10	8.6	2.3
OL2	9.0	2.2	15	5.5	6.2
OL3	8.2	3.7	14	5.5	0.50
OL4	4.9	1.0	<10	1.5	0.20
OL5	4.7	1.0	<10	1.0	0.70
OL6	8.0	3.5	16	9.5	-
OL7	15	5.7	22	6.0	-
OL8	1.9	<1.0	<10	2.0	-
OL9	3.0	<1.0	<10	3.1	-
OL10	<1.0	<1.0	<10	2.1	-

Table X

## GRAPHITE FURNACE ATOMIC ABSORPTION ANALYSES

## C O N C E N T R A T I O N S

Sample Identification	Ni ppm	Co ppm	V ppm	Cr ppm	Cd ppm
Phosphate A	-	20	53	-	3.4
B	-	2.0	100	-	7.5
C	-	7.5	73	-	6.5
Darahib Sulfide 1	14	9.6	32	12	400
2	61	6	25	28	2000
3	20	13	<25	8.5	650
4	37	7	100	30	2300
5	13	5	<25	9.3	720
Umm Samiuki, eastern emine Sulfide 1	8	3	<25	16	460
2	29	2	70	42	120
3	11	2	<25	25	970
4	21	2	65	22	90
5	19	<2	90	35	260
6	10	9	85	42	170
7	12	<2	45	32	420
Hamata Sulfide 1	9	11	<25	29	1300
2	12	32	260	29	2.3
Maakal Sulfide 1	35	18	80	60	1.9

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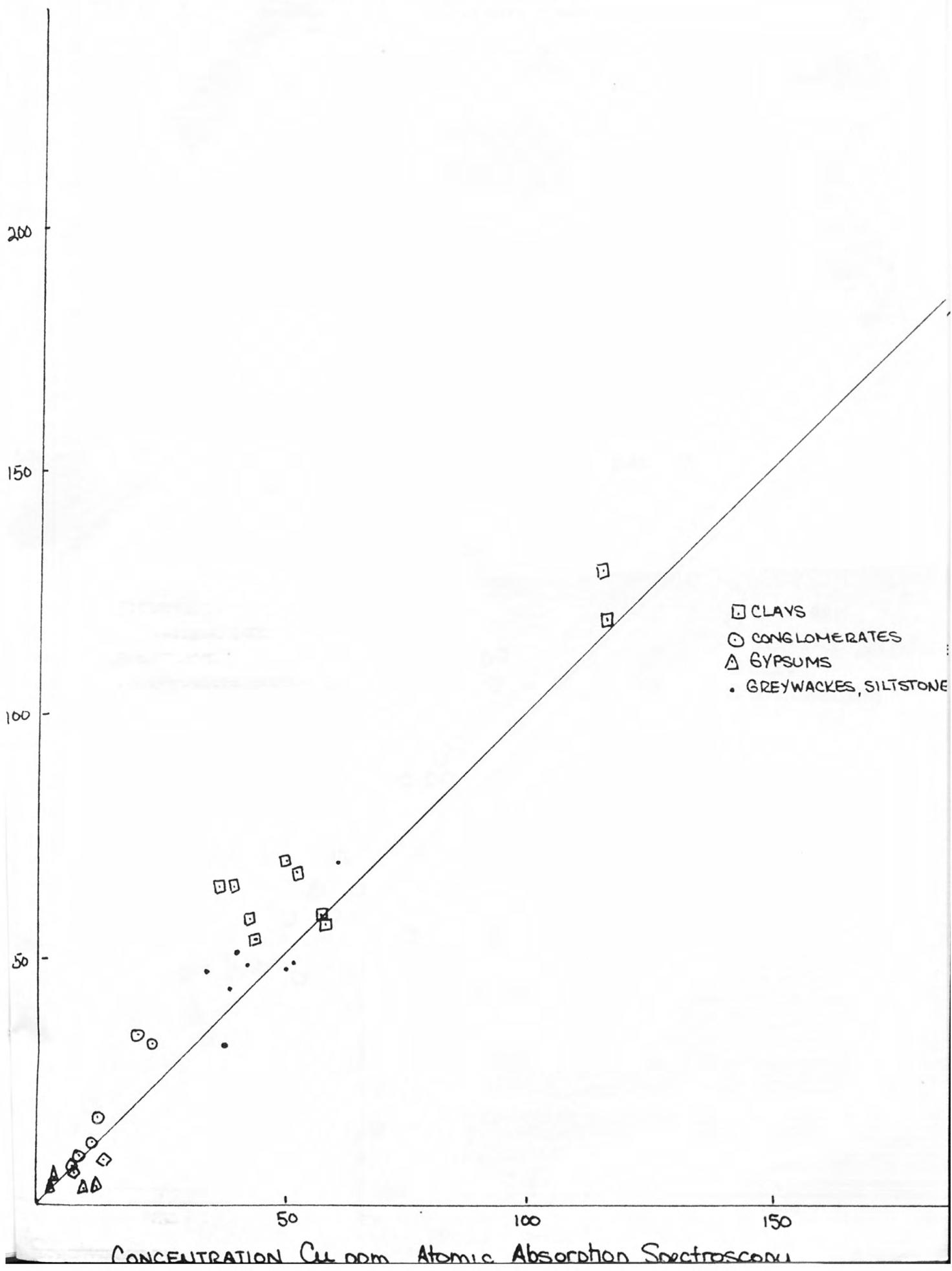


Figure 4 Zinc Correlation Plot

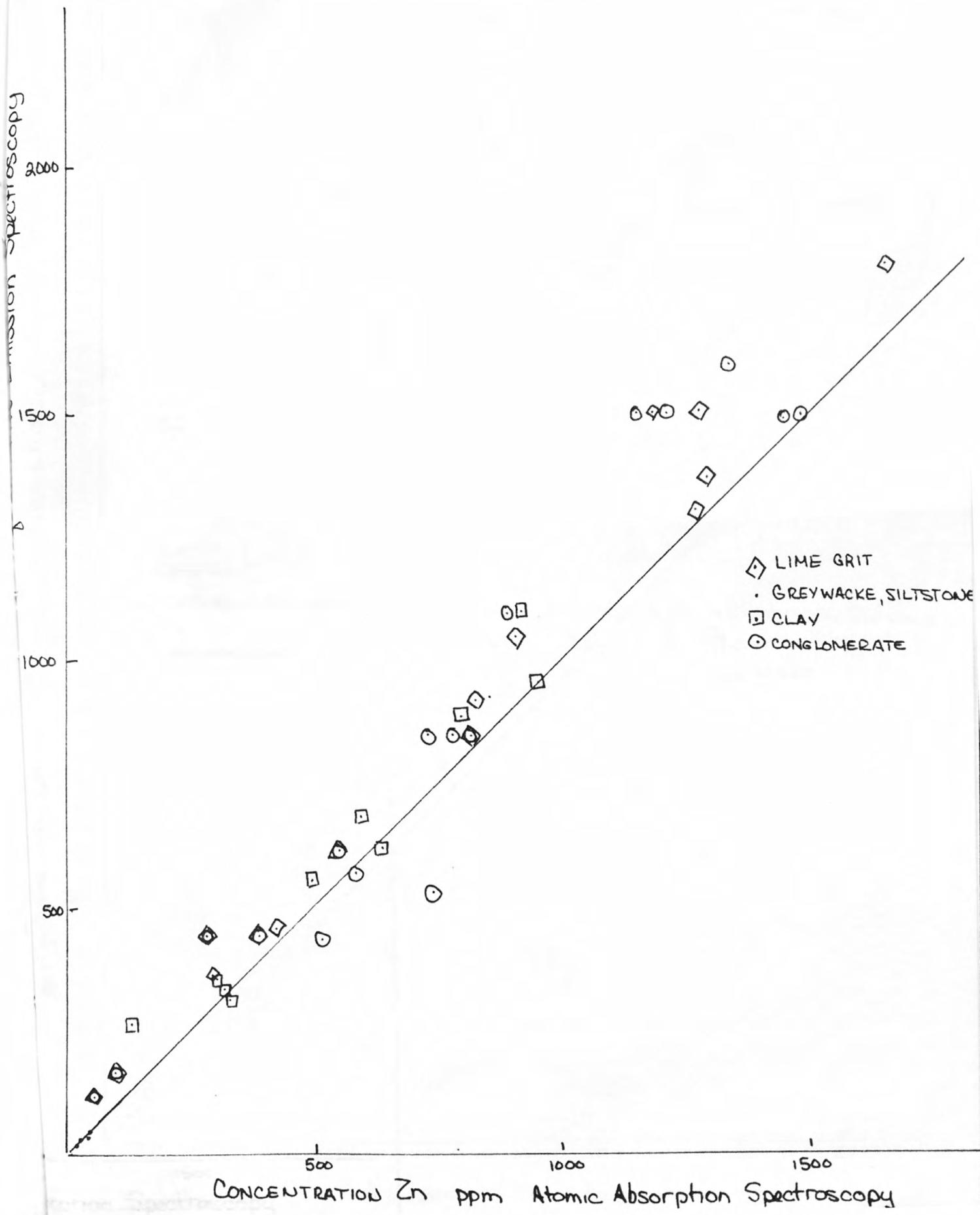
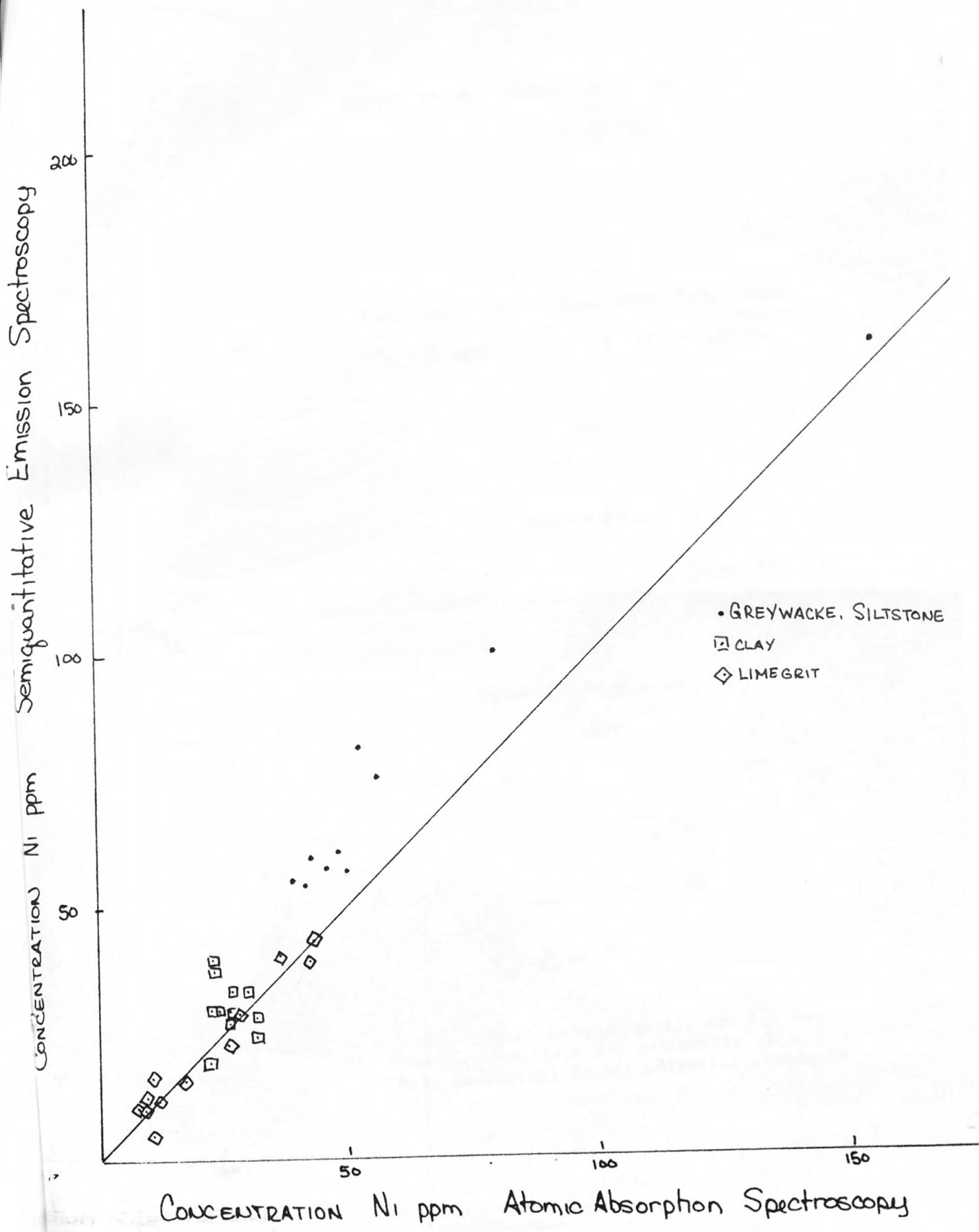


Figure 5

Nickel Correlation Plot

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