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TRACE METAL PRECONCENTRATION FROM GEOLOGICAL
SAMPLES FOR ANALYSIS BY X-RAY FLUORESCENCE

by

David R. Strait

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science - Geochemistry.

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ABSTRACT

Geochemists often require multiple trace element determinations from rock and water samples. X-Ray fluorescence (XRF), excellent for multielemental analysis, has poor sensitivity for trace elements and requires complex matrix-effect corrections. Preconcentration of trace elements into a uniform matrix eliminates disadvantages of trace element XRF analysis. Ethylenediamine functional groups, attached to controlled-pore glass beads by a silylation reaction, simultaneously preconcentrate Bi, Pb, Zn, Cu, Ni and Co by chelating the metals from water solution. Water samples adjust to pH eight and the metals preconcentrate by column extraction. Rock samples digest in hydrofluoric acid, then Dowex 50 cation exchange resin separates iron from the trace metals. The trace metals in water solution preconcentrate by batch extraction. A simple sample pellet preparation technique improves trace metal sensitivity four to twelve times compared to pressed or fused pellets. A molybdenum radiation enhancer behind the pellet and 75 mg pellets give optimum analyte line intensities. Precision for water analysis is 1.3 to 3.7 percent relative standard deviation with 200 ug each of the six metals. Rock sample precision for Zn, Cu, Ni and Co is 5.2 to 6.4 percent relative standard deviation and accuracy is usually good. Lead determinations are imprecise and inaccurate because of poor rock digestion and uncontrolled resin column flow rates. Linear standard calibration

curves replace matrix-effect calculations. With optimum instrument conditions, detection limits are 0.04 to 0.15 ppm for ten gram rock samples and 0.4 to 1.5 ppb for one liter water samples, which are adequate for many rock and water determinations. CaO and MgO concentrations over 15% in rocks interfere significantly with trace metal preconcentration. The method works well, but improvements can be made using a more complete rock digestion procedure and using solution pumps to control column flow rates. Several other metals can be preconcentrated using this procedure and use of Dowex 1 in the iron removal procedure allows anion preconcentration.

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INTRODUCTION

Geochemists often require multiple trace metal determinations from rock and water samples. X-Ray fluorescence (XRF) analysis, useful for multielemental determinations, has several disadvantages. First, XRF analysis is not very sensitive for trace metal analysis. Second, XRF analysis usually requires complex calculations to correct for matrix effects. Third, conventional sample preparation for XRF analysis decreases sensitivity for trace elements.

XRF detection limits for trace metals may range from 1 to 50 ppm sample concentration. The detection limit depends on the element, the matrix and the instrument. Rock and water samples often have metal concentrations below the detection limit, and metal determinations near the detection limit are imprecise and may be inaccurate.

Matrix effects in rock samples are very complex for XRF analysis. Accurate trace metal determinations require lengthy calculations to correct for the matrix effects. The matrix calculations require either much time or the expense of a computer.

Conventional sample preparation reduces the trace metal sensitivity for rock analysis. Many sample preparation techniques add a flux or a binder to the sample, resulting in trace metal dilution and decreased sensitivity. Sample preparation for water samples presents other problems. X-Rays striking the water sample may

initiate reactions at the solution-sample holder interface. The reactions may alter analyte concentration at the analyzing surface, resulting in inaccurate determinations.

Despite its problems, XRF analysis has several advantages. XRF analysis can be very accurate and precise if the concentration of the element is relatively high. It can determine many elements in a sample during a single run, and makes accurate determinations regardless of the elements' chemical state. Complete automation of the XRF spectrometer reduces operator time to the sample preparation. These advantages make XRF analysis an appealing method for multielement determinations. However, it is necessary to eliminate the disadvantages listed above, to make XRF analysis useful for trace metal determinations.

Trace metal preconcentration eliminates many of the objections of XRF analysis. Preconcentration increases trace element concentration by placing trace elements from a large sample into a small sample. The preconcentration of trace elements gives three distinct advantages over direct XRF analysis. The first, and most obvious advantage is that the preconcentrated sample has much higher trace metal concentrations than in the original sample. The higher trace element concentration allows determinations of metals that are below the detection limit in the original sample. Determinations of trace elements near the detection limit in the original sample become more precise and accurate when preconcentrated. The second

advantage of preconcentration is that water samples analyze as solids, eliminating solution reactions that yield unreliable results. The third advantage is the elimination of matrix effect calculations. The preconcentrated sample matrix is uniform for all samples, within the limits of measurement error. Preconcentration essentially eliminates analytical variation resulting from matrix effects.

Most preconcentration techniques have two major faults for geological analyses. First, they do not preconcentrate trace elements from both rock and water samples. Second, preconcentration methods for rock samples usually preconcentrate only one element at a time. This research results in a procedure that preconcentrates metals from both rock and water samples, allowing geochemists to analyze both types of samples by the same procedure. The procedure simultaneously preconcentrates Bi, Co, Cu, Ni, Pb and Zn, taking advantage of the XRF spectrometer's ability to analyze several elements during a single run. The sample pellet preparation method improves sensitivity by increasing the x-ray intensity on the sample, and decreasing x-ray absorption by the pellet matrix. Calculated detection limits are less than 0.3 ppm for Co, Cu, Ni, Pb and Zn using a 10 g rock sample, and less than three ppb using a 1000 ml water sample.

Previous preconcentration research and XRF theory as it pertains to the analysis of preconcentrated samples is reviewed, followed by four specific research phases:

- 1) Sample Pellet Preparation: preliminary research of the

sample pellet preparation, with a study of the effect of pellet thickness and the effect of a radiation enhancer.

2) Conditions Affecting Metal Ion Extraction: water solution pH and extraction time.

3) Extraction of Metal Ions from Water Solutions: precision studies, standard curves using batch and column type extractions, and detection limit calculations.

4) Rock Sample Analysis: precision and accuracy of the procedure using USGS rock standards, and the effect calcium has on the procedure.

Appendices give detailed laboratory procedures. Appendix I describes the immobilization of the chelating agent onto the glass bead surface. Appendix II describes the procedure to remove iron from rock samples. We describe the extraction of the ions onto the glass beads in Appendix III. Appendix IV shows how the glass beads prepare for analysis by making them into a sample pellet. Appendix V lists special materials and supplies used in this research, and ordering information.

PREVIOUS WORK

Preconcentration Using Ion-Exchange Resins

Previous investigations resulted in methods to preconcentrate trace metals from water solutions or rocks using ion-exchange resins. Preconcentration extracts metals from water solutions onto solids (liquid-solid extractions). The solid contains functional groups that extract metal ions from solution by mixing the solid with the solution (batch extraction), or by passing the solution through a column that contains the solid (column extraction).

Dingman et al. (1972) used batch and column extraction procedures to preconcentrate Co, Cu, Ni and Zn from synthetic sea water samples. Polyurea resin with amino functional groups extracted the metals, and HCl eluted the metals from the resin for analysis by atomic absorption spectrometry. Leyden et al. (1975a) used a similar procedure to preconcentrate Cu, Ni and Zn from sea water. Leyden pressed the resin into a pellet under high pressure for XRF analysis.

Blount et al. (1973) used ion-exchange resins to preconcentrate trace metals from rock samples. Prior to preconcentration, he digested the rock sample in acid to dissolve the trace metals for preconcentration by a liquid-solid extraction. Highly selective resins extracted the trace metals from solution by batch extraction. The selective resins reduced interference from major or minor

elements in rocks. However, the selectivity of the resins also limited the number of elemental species of trace elements preconcentrating on the resin.

Blount preconcentrated several trace metals from digested rock standards using a batch extraction procedure with the selective resins. NMRR resin preconcentrated gold from rock standards dissolved in dilute HNO_3 , and Chelex 100 extracted bismuth from dilute HNO_3 solution. The resins were pressed into pellets and analyzed by XRF. Blount also used Chelex 100 to preconcentrate cobalt and nickel from rock standards for XRF analysis. However, an iron spectral line overlaps the primary cobalt spectral line interfering with cobalt determinations. Blount resolved this problem by using an iron removal technique to separate the iron from cobalt and nickel, prior to preconcentration on Chelex 100. The EXPERIMENTAL section describes the iron removal procedure in detail.

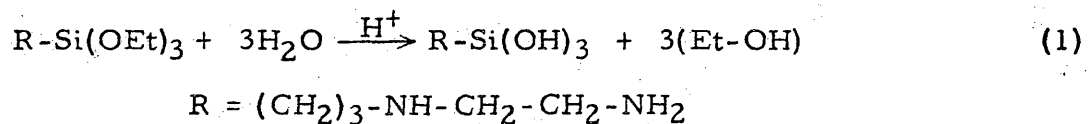
All of the preconcentration procedures listed above suffer several disadvantages. None of the procedures preconcentrate trace elements in both rock and water samples. Also, the rock preconcentration procedures will preconcentrate only one or two elements at a time and take up to 24 hours to equilibrate.

Preconcentration Using Chelating Group Immobilized on Silica Substrates.

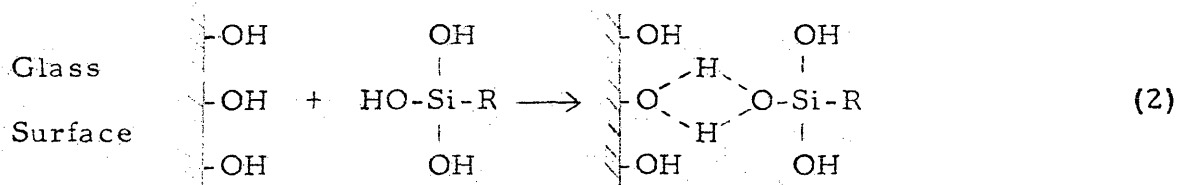
Leyden and Luttrell (1975b) introduced a significant advance in multielemental preconcentration using silane compounds attached to silica substrates. The silane compound has amino functional groups

(ethylenediamine) that chelate ions from solution. The functional groups attach to controlled-pore glass beads via a silylation reaction, which is described in general terms: Nitric acid activates the glass bead surface prior to the silylation reaction. Water washes acid from the activated beads, and they react with the silane compound in dilute acetic acid solution. The beads recover from solution by filtration. Water, toluene and isopropyl alcohol washes remove excess solution from the beads. The beads are stable under normal storage conditions after curing them at 80° C. Appendix I gives complete laboratory procedure for the silylation reaction.

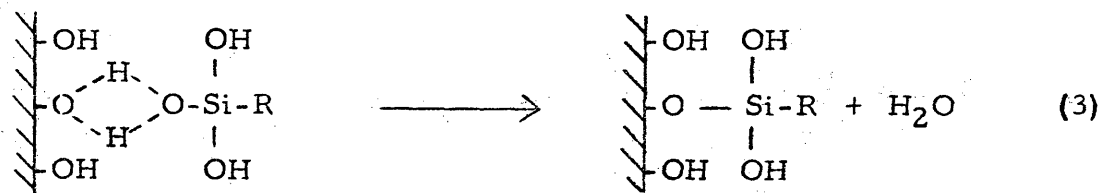
Silane compounds do not react directly with the glass surface. Hydrolyzing the silane compound is necessary before the silylation reaction is possible (Kahn, 1973). Equation 1 represents the acid catalyzed hydrolysis of a silane compound.



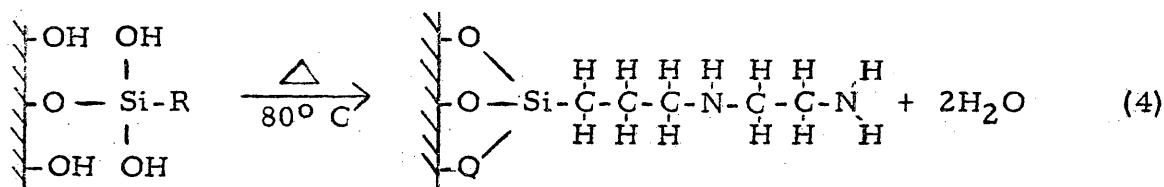
The hydrolyzed silane forms hydrogen bonds with a glass surface, as represented by equation 2.



The formation of covalent bonds attaches the silane to the glass surface, as shown in the reaction of equation 3.



Curing the mixture at high temperature completes the bond formation (Leyden, 1975b). Equation 4 represents the formation of permanent bonds.



The silylated glass is stable at room temperature, although the bonds may hydrolyze in solutions of high or low pH. Hydrolysis is not significant in solutions of pH between 3 and 10.

Diamine functional groups (equation 4) chelate both cations and anions. Anions are chelated below pH seven by the diprotonated diamine species, $(\text{H}_2\text{en})^{2+}$ (Leyden et al., 1976b). Leyden used silylated silica substrates with ethylenediamine functional groups to preconcentrate the oxyanions arsenate, dichromate, selenate, molybdate, tungstate and vanadate from standard solutions. Cations are usually chelated above pH seven, and probably have the form, $\text{cation}-(\text{en})_2^{2+}$ (Leyden and Luttrell, 1975b), with the cation coordinated

between two diamine groups. Leyden and Luttrell (1976a) used silylated silica substrates to preconcentrate cations of Ag, Cd, Co, Cr, Cu, Eu, Fe, Hg, Mn, Ni, Pb, and Zn from standard solutions, lake water and distilled water. After ion preconcentration, the silica substrates were mixed with a cellulose binder and pressed into pellets for XRF analysis.

Preconcentrating trace metals onto silylated silica substrates has some advantages over ion-exchange methods. The silylated substrates can preconcentrate a larger number of elemental species, and equilibrium times are minutes instead of hours. However, the above procedure does not preconcentrate trace metals from rocks.

X-RAY FLUORESCENCE SPECTROMETRY

The Characteristic Line Spectrum

An excited element emits unique x-rays that comprise its characteristic line spectrum. XRF analysis depends on the detection and measurement of the characteristic line spectrum. The characteristic line spectrum arises when a vacancy occurs in an inner electronic shell of an atom. A vacancy occurs when an electron absorbs an x-ray from an x-ray tube (primary x-ray). The increased electron's energy ejects it from the atom and creates a vacancy. An electron from a higher energy level fills the vacancy and emits an x-ray. The energy of the x-ray is equal to the difference in energy between the two electronic orbitals. The electron that fills the original vacancy causes another transition, resulting in a second x-ray emission. By this process, a single vacancy initiates several transitions and x-ray emissions. Each transition and corresponding x-ray photon is of an energy almost unique to a given element. Thus, it is possible to identify an element by the detection of its characteristic x-rays. Characteristic x-rays are called secondary x-rays when produced by incident primary x-rays.

Individual spectral lines are identified by an abbreviated Siegbahn notation system. The notation lists the symbol of the chemical element first. The series (K, L, M) in which the electron vacancy occurs, is given next. "Alpha", "beta", etc. is the last

notation and indicates the particular line in the series. The alpha line is usually the strongest for a given series. The notation "Ni K alpha" indicates the strongest line originating from a K shell vacancy in nickel.

Excitation

Inner electron shell vacancies may occur by various methods, but our primary interest is excitation by x-ray absorption. An electron will not absorb an x-ray that does not have sufficient energy to eject the electron from the atom. An electron in a given energy level requires an x-ray of a minimum photon energy to eject the electron. The minimum energy is known as the absorption edge energy, or just the absorption edge. Besides being the minimum energy for electron ejection, it is also the most efficient energy for electron absorption. As the energy of the photons increases beyond the absorption edge, the electron is less likely to absorb the photon, and create a vacancy. To create a maximum number of vacancies in a given energy level of an element, the energy of the incident x-rays should have the energy of the absorption edge. The primary x-ray intensity also affects the number of electron shell vacancies. The greater the primary x-ray intensity, of appropriate energy incident on the sample, the more likely a vacancy will occur. A large number of vacancies for a given element will produce a strong characteristic line spectrum and yield good sensitivity. Trace element

analysis requires high instrument sensitivity. To make the most reliable trace element determinations, we must enhance the instrument sensitivity through the selection of optimum x-ray energies and maximize the x-ray intensity on the sample.

X-Ray tubes most commonly provide the source of primary x-rays for XRF analysis. The tube contains a tungsten filament cathode and a metallic anode, with a potential of 40 to 50 kV between the cathode and anode. Electrons thermally emitted from the filament accelerate to the anode. The accelerated electrons may lose part or all of their energy through inelastic Rutherford scatter as they approach the high Coulombic field near the nuclei of the anode atoms. The scattered electrons release energy by the emission of x-rays. We refer to x-rays that originate from electron scatter as primary x-rays. The primary x-rays create an x-ray spectrum that we refer to as the continuous spectrum, or the continuum (Figure 1). The continuous spectrum has several characteristics. It comprises a continuous range of wavelengths (energies). A minimum wavelength (maximum energy) of zero intensity steeply rises to a maximum intensity. The intensity gradually drops from the intensity maximum toward longer wavelength x-rays. The minimum wavelength of the continuum results from an electron losing all of its energy at once by Rutherford scatter. The tube potential determines the electron's energy and consequently determines the wavelength minimum of the continuum. X-Ray intensity increases with tube potential, tube current

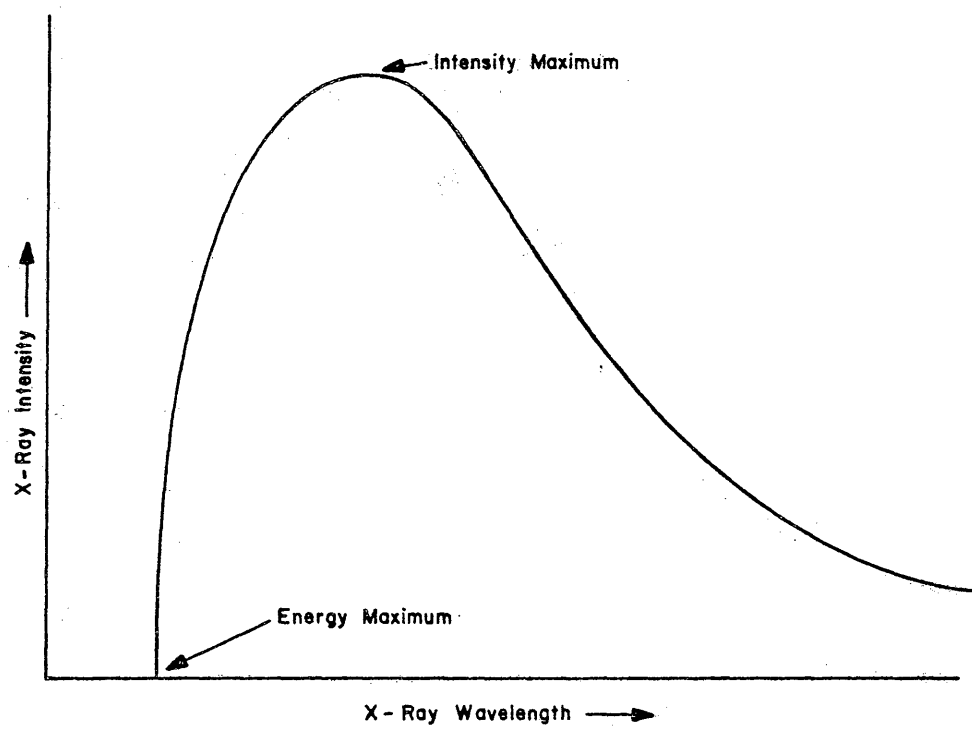


Figure 1 - Continuous spectrum of x-ray tube.

and with the atomic number of the anode material. Adjustment of tube potential, current and anode material gives the highest sensitivity for chosen trace elements.

Spectrum Dispersion

Wavelength dispersive XRF spectrometers use analyzing crystals to spatially separate the characteristic line spectrum into its component wave lengths. The dispersion by wavelength is necessary to measure each wavelength individually. The analyzing crystal diffracts incident x-rays from the surface of the crystal. A given wavelength will constructively interfere only at certain angles of diffraction, as given by the Bragg law:

$$n \lambda = 2d \sin \theta \quad (5)$$

where n is the order of the diffracted x-ray, λ is the wavelength of the x-ray and d is the distance between the diffraction planes of the analyzing crystal. The Bragg angle, θ , is the angle of diffraction at which constructive interference takes place. Complete destructive interference takes place at angles other than the Bragg angle. The destructive and constructive interference results in each wavelength being angularly separated. For a given order (n), the short wavelength photons constructively interfere at a lower angle than long wavelengths. The dispersion of the characteristic line spectrum by wavelength allows the individual measurement of a given wavelength.

Detection and Measurement of X-Rays

Wavelength dispersive spectrometers usually use two types of x-ray detectors. Proportional counters and scintillation counters detect individual x-ray photons. Proportional counters usefully detect long wavelength x-rays while scintillation counters usefully detect short wavelength x-rays. The analyzing crystal and detectors rotate relative to the x-ray beam in compliance with the Bragg law, to allow the detectors to scan the entire spectrum. The detectors translate the x-ray photons to electrical pulses, and a series of linear amplifiers amplify and shape the pulse. The pulse height analyzer (PHA) further shapes the pulse while eliminating pulses below and above chosen energies (voltages). The pulse height discrimination reduces background radiation and system noise and increases the signal-to-noise ratio, allowing greater instrument sensitivity for trace element analysis. After pulse height discrimination, the pulses pass to the scaler. The scaler counts the pulses as a function of time. The counts per unit time of a given analyte line is proportional to the concentration of that element in the sample.

Matrix Effects

The sample matrix influences the analyte line intensity by absorption-enhancement effects of the matrix. The matrix can absorb part of the primary (continuum) radiation. The absorption reduces the amount of primary radiation available to excite the analyte

and results in a decreased analyte spectral line intensity. The matrix can also decrease the analyte spectral line intensity by absorbing the analyte line. Enhancement of the analyte spectral line intensity results when the radiation from the matrix elements excite the analyte.

We can see absorption-enhancement effects by plotting standard curves. Figure 2 illustrates the standard curves of a two component system. Line A illustrates the standard curve for iron in a nickel matrix. The iron concentration ranges from 0 to 100%. The dotted line illustrates the line intensity we expect if there are no absorption-enhancement effects. The iron line intensity is substantially greater than we expect over much of the standard curve. The increase is due to enhancement by the nickel matrix. Line B illustrates the standard curve for nickel in an iron matrix. The dotted line again represents the curve we would expect if there were no matrix effects. The attenuation of the nickel line intensity is due to absorption by the matrix.

When the matrix composition includes several elements, absorption-enhancement effects become much more complex. Rock analysis may require consideration of ten or more major elements that comprise the matrix. The trace element determinations from rock samples involve complex calculations of those matrix effects. The problem becomes difficult for rocks because the matrix changes for each sample. It is necessary to calculate matrix effects for each rock sample.

Given a monochromatic incident primary beam, we can calculate

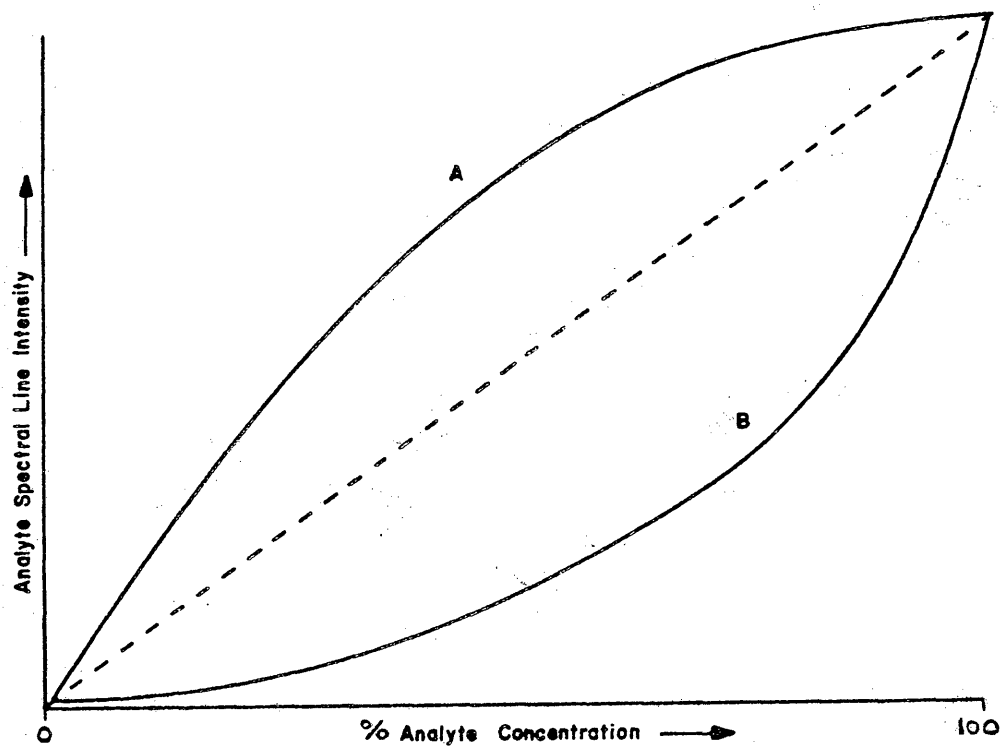


Figure 2 - Absorption-enhancement effects of a two component matrix. Line A is iron curve and B is nickel curve. Dotted line is expected curve if there was no absorption-enhancement effects.

the line intensity for a given analyte in a matrix by (Bertin, 1975):

$$I = I_0 P_A \frac{C_A u_A}{C_M K_M + \sum C_i K_i} \quad (6)$$

Where:

- I is the analyte-line intensity.
- I_0 is the incident primary radiation intensity.
- C_A is analyte concentration.
- C_M is the concentration of the major matrix element.
- C_i is the concentration of individual minor matrix elements, i.
- P_A is the excitation factor.
- u_A is the coefficient for the absorption of the primary radiation per mass of the analyte.
- K_M, K_i is the coefficient for the primary and secondary radiation absorption per mass of individual matrix elements; corrected for sample geometry.

We simplify equation 6 by holding I_0 constant. P_A is constant for a given analyte, matrix and spectrometer, and u_A is constant for a given analyte and incident primary spectrum. K_M and K_i are constant for a given matrix element, analyte, sample geometry and incident primary spectrum. Eliminating the constants,

$$I \propto C_A / (C_M + \sum C_i). \quad (7)$$

When the major matrix element concentration (C_M) is very large, the other matrix elements concentrations (C_i) are insignificant and

the analyte-line intensity (I) becomes

$$I \propto C_A/C_M. \quad (8)$$

If the analyte concentration (C_A) approaches 0% (trace element), the major matrix element (C_M) approaches 100% and becomes essentially constant. Thus, the line intensity (I) for a trace analyte in a constant matrix is

$$I \propto C_A \quad (9)$$

The relationship between a trace analyte concentration and analyte line intensity is direct and linear.

EXPERIMENTAL

Preconcentration Procedure

This experimental procedure simultaneously preconcentrates several trace metals from either rock or water samples. Trace metals preconcentrate onto a glass bead substrate containing chelating functional groups. The functional groups attach to the glass bead surface by a silylation reaction, as described in the PREVIOUS WORK section.

Prior to preconcentration, rock samples must have iron removed. The iron removal procedure is a modification of a procedure Danielsson and Ekstrom (1965, 1966) developed to separate trace cations from iron in steel samples. Blount et al. (1973) modified the procedure to remove iron from rock samples. The iron removal procedure begins by digesting the rock in acids, and then placing the digested sample in a dilute HF solution to complex the iron with fluoride. This HF solution passes through a column of Dowex-50 cation exchange resin which adsorbs the trace metal ions of interest, but does not adsorb the complexed iron. The metal ions elute from the resin with HNO_3 . The acid solution containing the metal ions evaporates, leaving water soluble nitrate salts of the metals. The salts dissolve in water. Having removed iron from the rock samples, the solution containing the cations is treated as a water sample.

Glass beads preconcentrate cations from water solution by

either batch or column extractions. The glass beads contain amino functional groups that chelate metal ions from water solutions. The amino functional groups chelate many metal ions, but do not significantly adsorb group I and II ions (Dingman, 1972 and Leyden, 1976a).

After extracting the ions from solution, the glass beads are prepared into pellets by recovering them from solution on filter paper. The filter paper and beads are inserted into a sample holder, with a radiation enhancer backing the sample in the holder. The radiation enhancer increases the x-ray intensity striking the sample during XRF analysis.

Description of Experiments

This investigation divides into four research phases, each comprising several experiments:

- 1) Sample Pellet Preparation. Experiments include preparation of the glass beads into pellets for XRF analysis. One experiment compared trace metal sensitivities resulting from the analysis of three pellet preparation techniques. This determined the pellet preparation technique yielding the highest trace metal sensitivity. Another experiment compared sensitivity of a pellet with a radiation enhancer with the sensitivity of a pellet without a radiation enhancer. A third experiment analyzed sample pellets of different thicknesses to determine the pellet thickness that yielded the highest trace metal sensitivity.
- 2) Conditions Affecting Metal Ion Extraction. These experiments

defined optimum conditions for the extraction of metal ions from solution with silylated glass beads by the batch extraction procedure. Metal ions preconcentrated from solutions of various pH determined the extraction efficiency of the glass beads as a function of pH, and the optimum pH for multielemental preconcentrations. A second experiment extracted metal ions by the batch method using various mixing times to determine the mixing time for maximum cation extraction.

3) Extraction of Metal Ions from Water Solutions. These experiments quantified the ability of the glass beads to preconcentrate trace metal ions from water solutions. One experiment determined the precision of the water analysis procedure by preconcentrating several identical standard metal ion solutions. Standard curves were made from the analyses of standard metal solutions preconcentrated by batch and column extraction techniques. The batch extraction standard curves provided data for detection limit calculations.

4) Rock Sample Analysis. These experiments investigated trace metal preconcentration from rock samples determining the type of rock samples for which the preconcentration procedure is useful. Trace metals preconcentrated from several USGS rock standards determined the precision and accuracy of the preconcentration procedure as applied to rock analysis. Metal ions preconcentrated from standard solutions containing

high concentrations of calcium ion determined the effect of calcium on trace metal preconcentrations.

X-Ray Instrument and Measurement Parameters

All x-ray measurements were made on a Philips model PW-1410 spectrometer, modified for complete computer automation. All elements were determined using a LiF-200 analyzing crystal except zinc, which used a LiF-220 analyzing crystal. A gas (10% methane, 90% argon) flow proportional counter was used in tandem with a scintillation detector, for x-ray detection. A chromium-anode x-ray tube was operated at 45 kV and 35 mA, using a Philips XRG-2500 full wave x-ray generator.

The same spectral line was consistently measured for a given element throughout this research. The L alpha line was measured for Bi and Pb and the K alpha line for all other elements. Hereafter, the spectral line is usually identified only by the element symbol. Each metal ion analyzed has the 2^+ oxidation state, except for bismuth, which has the 3^+ oxidation state. Each analyte intensity is given as peak minus background intensity. The intensities were measured as counts per unit time, scaled for presentation to counts per second (cps). The counting times were limited to 100 seconds, or less. If less than 100 seconds, the counting time was long enough to give an accuracy of 1% relative standard deviation. Throughout this research, the instrument (PHA, detector voltages, etc.) settings were varied

for different experiments. Identical samples may yield different intensities because of different instrument settings, sometimes preventing direct comparison of line intensities among some of the experiments. For some experiments, such as the rock analysis and the standard curves, the instrument settings were the same.

SAMPLE PELLET PREPARATION

Comparative Study of Three Pellet Preparation Methods

This experiment investigated three pellet preparation techniques to determine a method that yields high sensitivity for trace metals. Two of the methods have been used previously in this and other laboratories for rock analysis. Both previously used methods require the addition of large quantities of binder or flux to the glass beads to form a pellet, decreasing analytical sensitivity by absorbing primary and secondary radiation. The new pellet preparation technique, specifically for preconcentrated samples, requires no additional matrix.

The new pellet preparation technique was compared with the other two pellet preparation methods to determine which method yields the greatest sensitivity for trace metals. Three identical glass bead samples prepared by the batch extraction method. Appendix III details the batch extraction procedure. Ten milliliters of standard solution, made with nitrate salts of six metals, were added to each

of three beakers. The standard solution contained 200 ug each of Bi, Pb, Zn, Cu, Ni and Co, buffered to pH eight with a phosphate buffer. One hundred mg of silylated glass beads were added to each solution, stirring the mixtures for ten minutes. The beads collected on 25 mm filter paper, then dried on the filter paper in a 105° C oven.

Each of the three glass bead samples were made into pellets. One pellet was prepared by removing the glass beads from the filter paper, mixed with six grams of lithium tetraborate on a mixing wheel for four hours. The mixture fused in a Claisse fluxer at 1100° C to yield a 1 1/4 inch diameter fused pellet. A second pellet was made by removing the glass beads from the filter paper, and grinding them with three grams of boric acid for 45 minutes in a Spex ball mill. The mixture, placed in an aluminum sample cup, was pressed at 10,000 p. s. i., forming a 1 1/4 inch diameter pressed pellet. The pressed and fused pellet techniques are standard pellet preparations for rock analysis in this laboratory. The final glass bead sample was prepared by a method referred to as the no-matrix pellet. Appendix IV details the no-matrix pellet preparation. The beads, with filter, were placed onto a metal support disk. A thin polypropylene film covered the support disk and glass beads. The entire apparatus inserted into a sample holder slide, with the support disk and polypropylene film sandwiching the beads and containing them in the sample holder slide. The pellets analyzed by XRF and the analyte line intensities were compared to determine which pellet gave the highest trace metal sensitivity.

Sample Holder Radiation Enhancer

A radiation enhancer was used to increase the analyte spectral line intensity of the no-matrix pellet. The enhancer was made with a molybdenum disk that inserts between the sample support disk and the glass bead sample pellet (see Appendix IV). An enhancer should increase the x-ray intensity from elements in the sample, because the thin sample pellet absorbs only part of the incident radiation from the x-ray tube, the remainder passing through the pellet. The molybdenum enhancer absorbs the radiation passing through the sample, causing the enhancer to fluoresce. The x-ray emissions from the enhancer strike the sample pellet, causing the sample to fluoresce.

To test the molybdenum radiation enhancer, two identical glass bead samples were prepared by the batch extraction procedure. Twenty milliliters of standard metal solution, containing 100 ug each of Bi, Pb, Zn, Cu, Ni and Co, were placed in each of two beakers. To the solutions, buffered to pH eight, 100 mg of silylated glass beads were added and the mixtures stirred for ten minutes. The glass beads were made into pellets, one pellet with a molybdenum (99.95% pure) radiation enhancer, the other pellet with an aluminum (99.999% pure) backing plate. The aluminum characteristic line spectrum does not excite any of the elements' lines measured, so the aluminum backed sample has no enhancement. The analyte spectral line intensities were measured for each pellet by XRF to determine the effect of the molybdenum radiation enhancer.

Effect of Pellet Thickness

The thickness of the no-matrix pellet was adjusted to increase the analyte spectral line intensity. Several no-matrix pellets were prepared, each containing the same concentration of copper but of different thickness. The pellet diameter and glass bead density remains constant making pellet thickness a function of pellet mass. Pellet thickness was measured indirectly by measuring the glass mass. Each pellet analyzed by XRF to determine the effect pellet thickness has on analyte line intensities.

Five 10 ml standard solutions that contained 50, 100, 150, 200 and 250 ug copper were buffered to pH eight. To each solution, 50, 100, 150, 200 and 250 mg of silylated glass beads were added respectively, and the mixtures stirred for ten minutes. Pellets made from the beads had a 1000 ppm copper concentration, but each pellet contained different masses of copper. XRF analysis measured the Cu K alpha line intensity to determine the pellet thickness yielding the highest copper line intensity.

CONDITIONS AFFECTING METAL ION EXTRACTION

Extraction as a Function of pH

Solution pH controls the amount and rate of cation extraction by the silylated glass beads (Leyden and Luttrell, 1975b). We performed an experiment to determine the solution pH for fastest cation extraction rates. A set of several identical standard

solutions were adjusted to various pH values. Silylated glass beads extracted cations from the solutions, but the beads were removed from solution before extraction reached equilibrium. Analysis of these samples showed which pH allows rapid cation extraction.

A second experiment determined the pH for maximum cation extraction, or the most efficient extraction pH. A set of solutions, identical to the first set, mixed with silylated glass beads until the extraction reached equilibrium, showed which pH allows greatest cation extraction.

Each set of samples were prepared by placing fifty ml of standard solution, containing 200 ug each of Bi, Pb, Zn, Cu, Ni and Co, in each of eight beakers. Dilute NaOH and HNO₃ adjusted the pH of each solution to one of the following values: 3, 4, 5, 6, 7, 8, 9 or 10, ± 0.1 pH. The unequilibrated solutions stirred with 100 mg of silylated glass beads for five minutes, and the equilibrated set stirred for 40 minutes. Pellets prepared from the samples were analyzed by XRF.

Extraction as a Function of Time

This experiment determined the mixing time that the batch extraction procedure requires to reach equilibrium. For consistent analytical results the beads must mix with the solution long enough for the extraction to reach equilibrium.

Several standard solutions were prepared containing equal masses of three trace cations. To these solutions, silylated glass beads were added and the mixtures stirred for different periods of time. Pellets made from the glass beads were analyzed by XRF. The line intensities, proportional to the amount of metal extracted for each mixing time, determined which mixing time gives the most complete extraction of metals.

Fifty milliliters of standard solution containing 200 ug each of Pb, Zn and Co was added to each of six beakers. The solutions buffered to pH eight and 100 mg of silylated glass beads were added to each beaker. The six mixtures stirred for various time periods of 0, 1, 3, 5, 10, and 15 minutes. For the mixing time of zero minutes, the beads were added to the solution and immediately poured into a filtering flask to recover the beads. The solution takes about 30 seconds to pass through the filter, allowing trace metal extraction. Pellets made from the beads were analyzed by XRF.

EXTRACTION OF METAL IONS FROM WATER SOLUTIONS

Precision Study

The total reproducibility of the batch extraction and XRF analysis was determined for cations preconcentrated from water solutions. Several standard metal ion solutions were preconcentrated,

holding the amount of metal, the solution pH, and the mixing time constant. Pellets prepared from the glass beads analyzed by XRF. The degree of variation in analyte line intensities indicated the precision of the procedure.

Five 50 ml solutions containing 200 ug each of Bi, Pb, Zn, Cu, Ni and Co were placed in separate beakers and buffered at pH eight. To each solution, 100 mg of silylated glass beads were added and stirred for ten minutes. Pellets made from the samples analyzed by XRF.

Standard Curves

Standard curves were made to test the linearity of analyte line intensity versus metal mass. Several solutions, each containing different amounts of metal ion, preconcentrated by batch and column extractions. Pellets made from the beads analyzed by XRF. Plotting analyte line intensity versus the metal mass originally present in the standard solution, a straight line was made from the points by a least squares linear regression. The line having the form

$$C_n = (I - b)/m, \quad (10)$$

where:

- C_n is the metal mass (ug).
- I is the analyte line intensity (cps).
- b is the background intensity (cps).
- m is the slope of the line, or sensitivity (cps/ug).

The linear regression determined the values for b and m for each metal ion.

Supplying b , m and I to equation 10 allows metal determinations for unknown samples. Including the original sample mass (G), converts metal mass (C_n) to metal concentration (C). Equation 10 becomes:

$$C = (I - b) / mG, \quad (11)$$

where the original sample mass (G) is given in gram units for rock samples, and the concentration (C) becomes $\mu\text{g/g}$, or ppm. For water samples, G is given in units of kg (or liters) and C is in ppb.

Standard curves for samples containing metals in the ppm range were made by batch extraction, and samples containing metals in the ppb range were made by column extraction. Batch extraction samples prepared by adding 50 ml of standard solution to each of seven beakers. The standard solutions contained Ni and Co ranging from 3 to 60 μg , Pb and Cu ranging from 10 to 200 μg , and Zn ranging from 25 to 500 μg , representing ratios of metals expected in rock samples. The solutions buffered to pH eight, 100 mg silylated glass beads were added to each beaker, and the mixtures stirred for ten minutes. Pellets made from the glass beads analyzed by XRF. Five samples were prepared by the column extraction method, using 250 ml of standard solution for each sample. The standard solutions contained 6.25 to 125 μg each of Bi, Cu, Ni, Co and Zn and buffered to pH eight. The solution passed through a column containing 100 mg

of silylated glass beads at a flow rate of about 20 ml per minute.

Pellets were prepared and analyzed by XRF.

Detection Limits

Detection limits were calculated with data obtained from batch extraction standard curves, using equation 12 (Bertin, 1975).

$$C_{DL} = (3/m)(I_B/T)^{0.5} \quad (12)$$

C_{DL} is the minimum concentration of metal detectable in the sample, I_B is the background intensity in cps, T is the counting time (seconds) and m is the slope (sensitivity) of the standard curve. Equation 12 determines the theoretical detection limit with a 95% probability that the analyte spectral line peak is actually present.

I_B was obtained from analyses made for the standard curves. The background intensity for the standard curves (b , equation 10), differs from the background intensity of the analysis (I_B); I_B is the background noise near the analyte line and is much larger than b . The standard curves give the slope (m). T is the maximum peak or background counting time allowed during the analysis and equals 100 seconds in these calculations.

ROCK SAMPLE ANALYSIS

Preconcentration of Rock Standards

Trace metals preconcentrated from several USGS rock standards determined the precision and accuracy of the procedure for rock

analysis. The previous precision study of water solutions is not valid for preconcentrating trace metals from rocks. Rock preparation includes an ion-exchange procedure to separate iron from the trace elements, and the major and minor elements in rocks might affect the preconcentration procedure.

Trace metals preconcentrated from four samples of andesite (USGS standard AGV-1), using batch extraction, determined rock analysis precision. Analyte line intensities were converted to metal concentration by equation 11. The precision of the preconcentration procedure and XRF analysis was determined from the metal concentrations.

Preconcentrating trace metals from four different USGS rock standards, including andesite (AGV-1), basalt (BCR-1), granodiorite (GSP-1), and peridotite (PCC-1) determined the accuracy of the rock analysis procedure. The analyte line intensities were measured by XRF, again converting the intensities to metal concentration using equation 11. The analyzed metal concentrations were compared with values in the literature (Flanagan, 1969), to determine the accuracy.

The iron was removed from the samples (see Appendix II) prior to preconcentration. One gram portions of the powdered standards digested in a solution of concentrated HNO_3 , HClO_4 and HF . The acids evaporated, leaving a residue. The residue, dissolved in 1N HF , passed through a column containing Dowex-50 cation

exchange resin which adsorbs Pb, Zn, Cu, Ni and Co. Dilute HF rinsed the column free of iron, then the metals of interest eluted from the column with 4N HNO₃. The solution evaporated on a hot plate, leaving a residue containing the nitrate salts of the metals. The salts dissolved in water and the solution adjusted to pH eight. One hundred milligrams of silylated glass beads were added to the water solution, and the mixture stirred for 10 minutes. Pellets made from the glass beads were analyzed by XRF and analyte line intensities converted to sample concentration using standard curves.

Effect of Calcium

The ion-exchange resin used to remove iron adsorbs calcium. Large amounts of calcium in rocks can interfere with the preconcentration procedure. This experiment determines how much calcium can be in a rock without interfering with trace metal determinations.

Several standard solutions were made containing equal masses of six trace metals. Different amounts of calcium ion were added to each solution and the trace metals preconcentrated according to the rock analysis procedure (Appendixes II - IV), except the rock digestion was eliminated. The x-ray line intensities showed how much calcium may be present in a sample without seriously affecting the analytical results.

Seven 50 ml 1N HF solutions were prepared, each containing 200ug of Bi, Pb, Zn, Cu, Ni and Co. To each solution except one,

various amounts of calcium nitrate was added. The amount of calcium added was calculated as percent CaO, adjusting the percent CaO to a sample size of one gram. Thus, for a 10% concentration of CaO, the equivalent amount of $\text{Ca}(\text{NO}_3)_2$ was added to yield 0.1 g of CaO. The amount of CaO added to the solutions ranged from zero to 30%. The solution passed through the resin column, followed by the standard rock preconcentration and analysis procedure.

RESULTS

SAMPLE PELLET PREPARATION

Comparative Study of Three Pellet Preparation Methods

Table 1 lists analyte spectral line intensities for three pellets that contain metal ions preconcentrated onto glass beads. Each pellet was made by a different pellet preparation method. The glass beads were fused with lithium tetraborate in one pellet. In another pellet, the glass beads were mixed with boric acid and pressed into a sample cup. The last sample was prepared by the no-matrix method. Each pellet contained 200 ug of each metal, so the analyte line intensities represent the relative sensitivity for each pellet preparation method.

The no-matrix pellet yields substantially higher analyte line intensities than the fused or pressed pellets. We calculated the percent intensity of the pressed and fused pellets, as compared to the no-matrix method.

Sample Holder Radiation Enhancer

Table 2 lists the analyte spectral line intensities for two pellets with different radiation enhancers. The energy of the principal (K alpha) emission line of each enhancer and analyte excitation potential is given in KeV. The excitation potential is the minimum x-ray photon energy a given element requires for excitation. From

Table 1 - Spectral line intensities for three sample pellet preparations. Values in parentheses represent the percent intensity of the no-matrix method.

		INTENSITY (cps)		
		Pressed Pellet	Fused Pellet	No-Matrix Pellet
Metal	Bi	34 (27)	22 (17)	126
	Pb	33 (14)	26 (11)	238
	Zn	57 (20)	31 (11)	291
	Cu	202 (27)	106 (14)	735
	Ni	86 (13)	52 (8)	650
	Co	98 (16)	49 (8)	620

Table 2 - Analyte line intensities for aluminum and molybdenum radiation enhancers.

INTENSITY (cps)				
	Excitation Potential (KeV)	Al K alpha =1.487 KeV	Mo K alpha =17.425 KeV	% increase with Mo enhancer
Bi	13.424	75	84	+ 12
Pb	13.044	80	90	+ 13
Zn	9.660	119	129	+ 8
Cu	8.980	324	380	+ 17
Ni	8.331	329	351	+ 7
Co	7.709	317	343	+ 8

Table 2, we see the Al K alpha emission line has a lower energy than all analyte excitation potentials. The aluminum enhancer can not increase analyte spectral line intensity by secondary fluorescence. The Mo K alpha emission line is energetic enough to excite all analytes. As expected, the molybdenum enhancer increases spectral line intensities for all analytes. The percent increase in analyte spectral line intensity for the molybdenum enhancer is given in Table 2.

Effect of Pellet Thickness

Figure 3 plots the Cu K alpha line intensity versus pellet mass. The intensity of the copper line for each pellet mass is given in parentheses. The pellet and copper mass is different for each pellet, but the copper concentration is constant (1000 ppm). The pellet mass is proportional to pellet thickness.

Figure 3 illustrates the effect pellet thickness has on analyte line intensity. The intensity initially increases linearly to a pellet mass of about 75 mg (A, A'), then the rate of intensity increase decreases. A pellet mass of 75 mg (or less) gives the highest copper sensitivity. For pellet masses above 75 mg, the matrix absorbs the primary and secondary radiation significantly. The intensity continues to increase to a pellet mass of 200 mg, due to increasing copper mass. Beyond a pellet mass of 200 mg, x-ray absorption by the matrix becomes severe enough to reduce the efficiency of the radiation enhancer, so the intensity decreases.

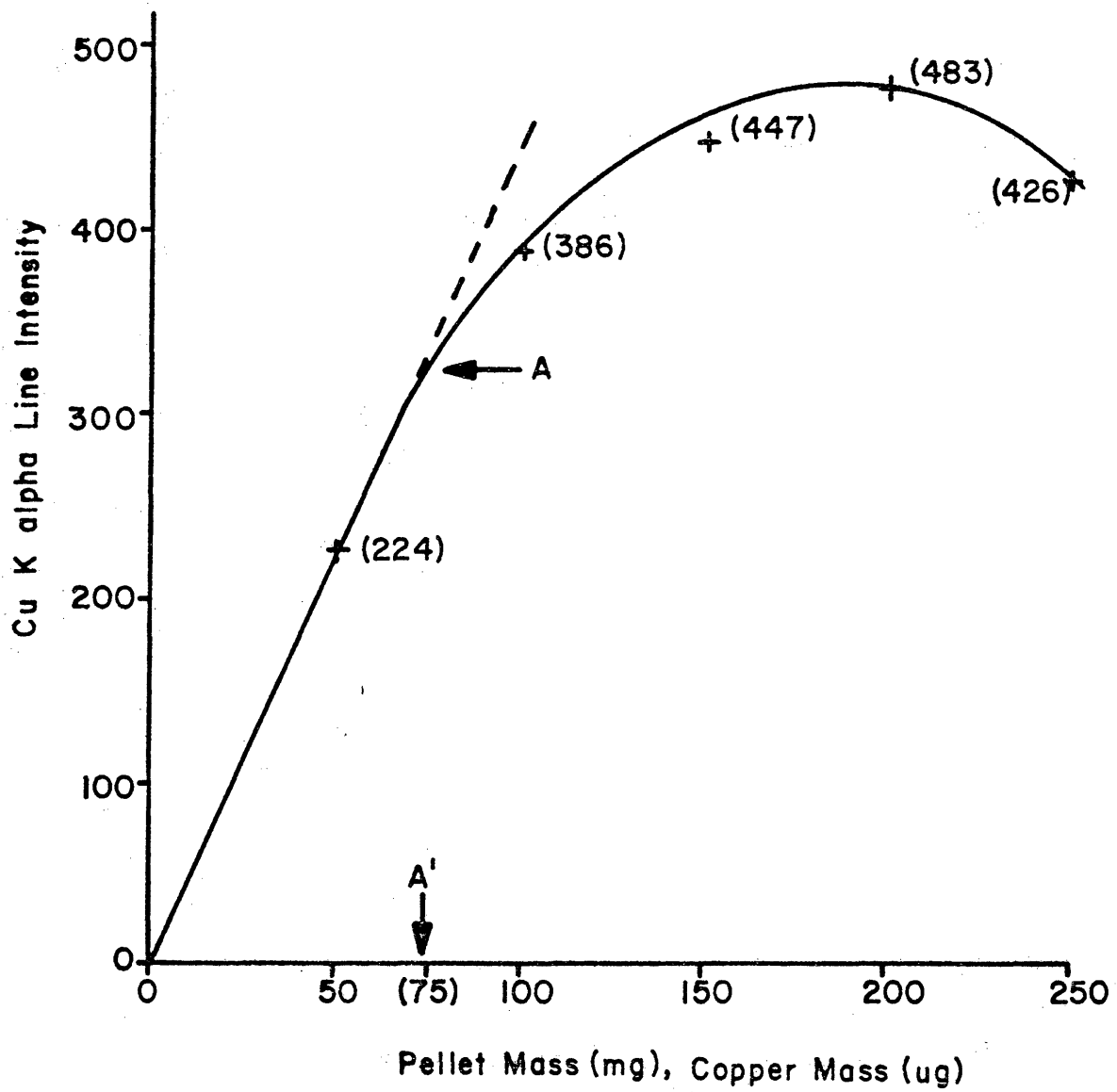


Figure 3 - Cu-K alpha line intensity versus pellet mass.
Each pellet contains 1000 ppm copper concentration.

CONDITIONS AFFECTING METAL ION EXTRACTION

Extraction as a Function of pH

Table 3 gives analyte line intensities for metals extracted at various pH and two mixing times. The intensities are normalized as a percent of the maximum intensity for a given analyte.

The five minute mixing time data represents an unequilibrated extraction and illustrates which pH yields the fastest extraction rates for each cation. The average normalized intensity for all elements is also listed for each pH. The highest average (84%) occurs at pH 8 and 10, and the second highest (78%) at pH 9, indicating the pH range yielding rapid multielemental extraction rates is between 8 and 10. The five minute extraction data is plotted in Figure 4 as percent of the maximum intensity versus solution pH.

Table 3 also lists normalized intensities for 40 minute extractions, representing an equilibrated extraction. The equilibrated extraction shows which pH yields the most complete or efficient extractions. Again, the average normalized intensities are listed for each pH. The most complete multielemental extractions occur at pH 8 and 9, yielding a 95 and 98 percent average, respectively. The extraction curves for 40 minute extractions are plotted in Figure 5.

Table 3 - Normalized analyte line intensities for batch extractions in various solution pH. Five minute (unequilibrated) extraction data and 40 minute (equilibrated) extraction data is given.

		INTENSITY Normalized to 100% Maximum								
		Five Minutes Mixing								
		Solution pH								
		3	4	5	6	7	8	9	10	
Metal	Bi	29	100	94	64	75	74	80	98	
	Pb	1	7	18	47	87	100	59	78	
	Zn	2	7	21	42	69	100	87	88	
	Cu	48	70	85	69	54	74	100	95	
	Ni	1	5	7	19	26	55	95	100	
	Co	1	7	18	41	57	100	51	44	
	*	14	33	41	47	61	84	78	84	
			Forty Minutes Mixing							
	Bi	30	24	26	27	50	89	96	100	
	Pb	2	1	69	75	70	96	100	71	
	Zn	1	5	56	79	93	93	94	100	
	Cu	52	76	73	74	62	97	95	100	
	Ni	1	3	22	42	51	97	100	89	
	Co	1	4	33	51	62	98	100	73	
*	15	19	47	58	65	95	98	89		

* Average normalized intensity for all elements at a given pH and mixing time.

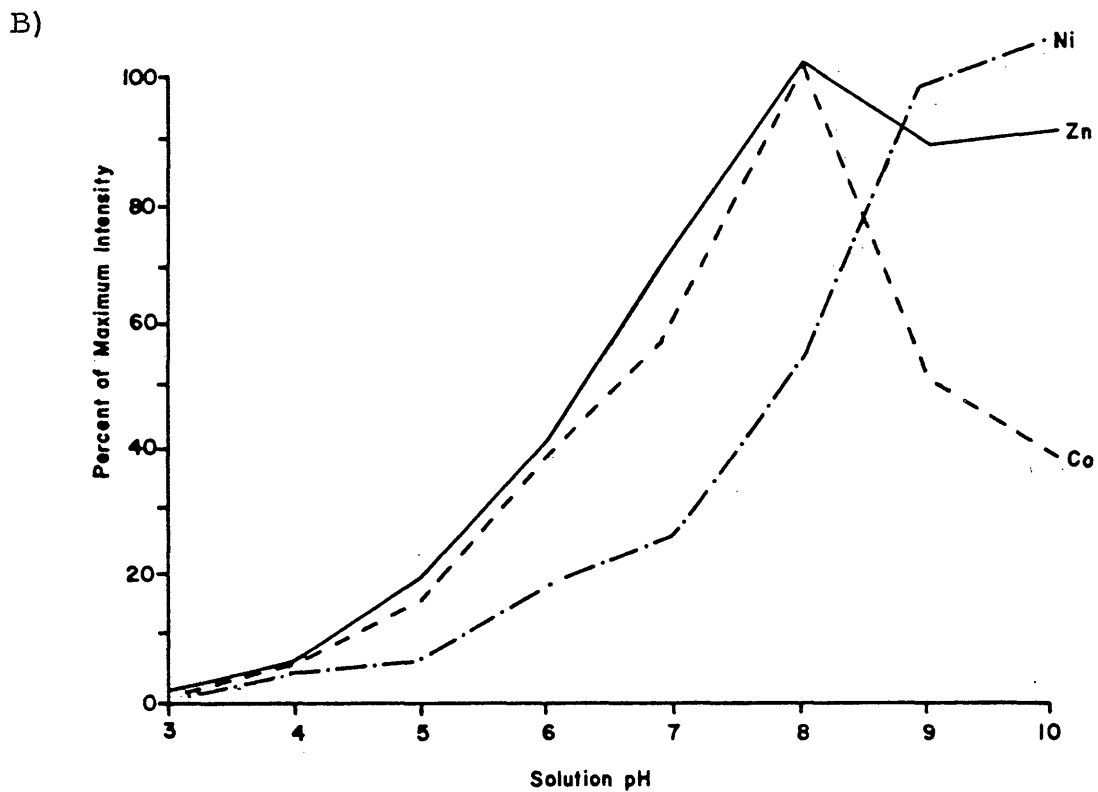
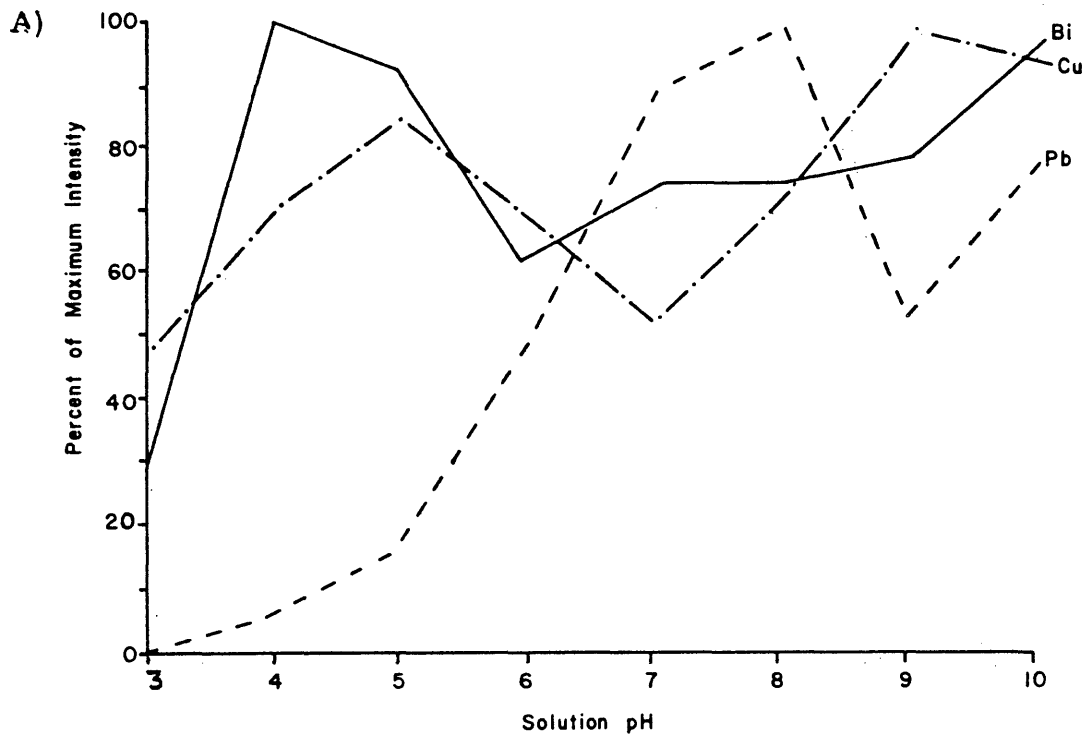


Figure 4 - Unequilibrated (five minute mix) pH extraction curves for extraction efficiency study. A) Bi, Pb and Cu, B) Zn, Ni and Co.

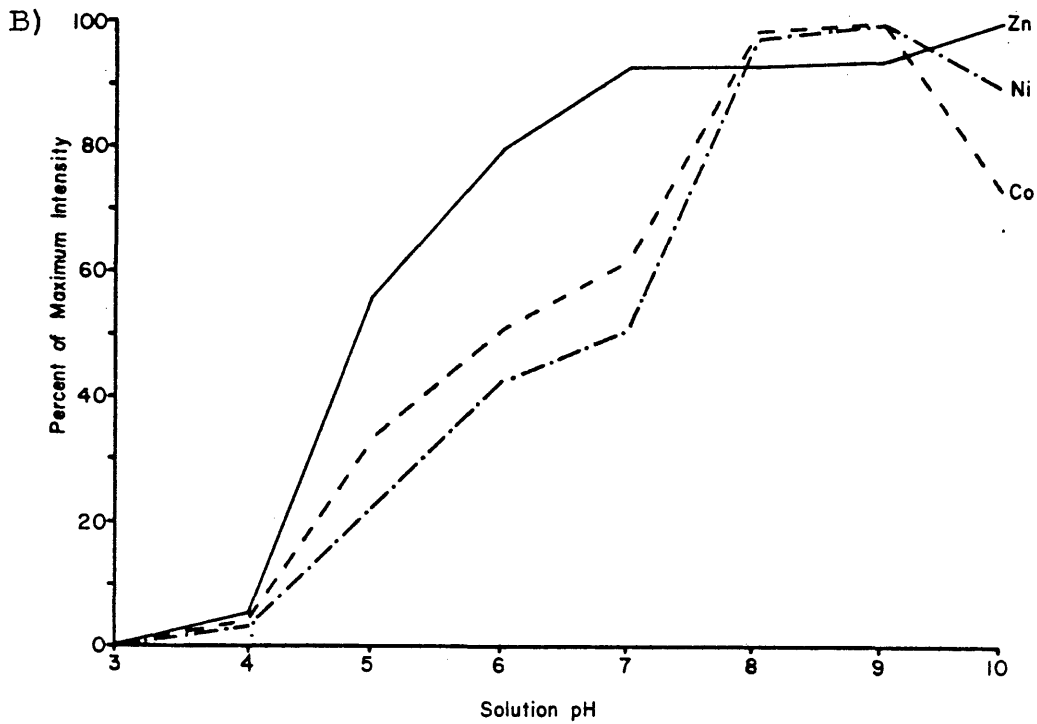
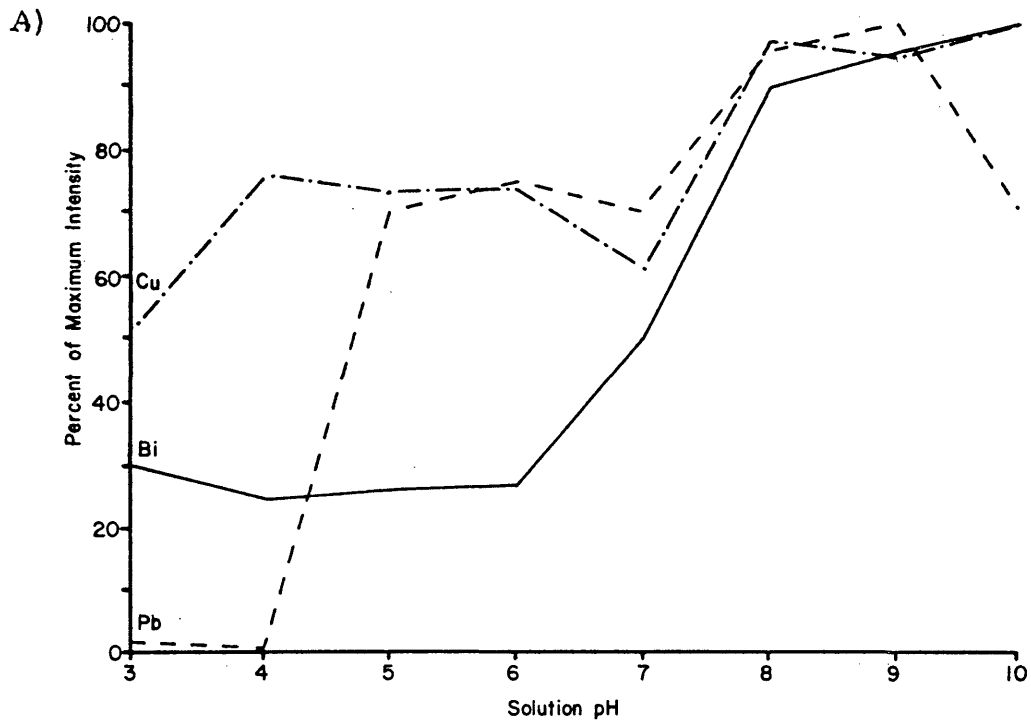


Figure 5 - Equilibrated (forty minute mix) pH extraction curves for extraction efficiency study. A) Bi, Pb and Cu, B) Zn, Ni and Co.

Extraction as a Function of Time

Table 4 lists the analyte spectral line intensities for the various batch extraction mix times at a solution pH of eight. The data is normalized as percent of the maximum count rate for each analyte, and is presented in parentheses. Silylated glass beads mixed with standard solutions containing 200 ug each of three metal ions. The beads extracted the ions from solution over a period of time ranging from zero to 15 minutes.

The line intensities generally increased with time until the extraction reaches equilibrium, at about ten minutes. All metals reached 99% maximum extraction at ten minutes mixing. Pb and Zn are extracted more completely than Co with no mixing and reach maximum extraction ten minutes sooner than Co. Zn and Co continue to have high intensities at 15 minutes mixing, while Pb intensity decreases. Optimum multielemental extraction mixing time is ten minutes for these three metals.

EXTRACTION OF METAL IONS FROM WATER SOLUTIONS

Precision Study

Table 5 lists the precision data obtained from the analysis of five preconcentrated water solutions, each solution containing 200 ug of each metal ion. The batch extraction method was used for each sample, with a solution of pH eight and mixing time of ten

Table 4 - Spectral line intensities for various batch extraction mix times. Data normalized as percent maximum analyte intensity is in parentheses.

		INTENSITY (cps)					
		Mixing Time (minutes)					
		0	1	3	5	10	15
Metal	Pb	211 (93)	213 (94)	210 (93)	226 (100)	223 (99)	213 (94)
	Zn	238 (83)	255 (89)	249 (86)	288 (100)	286 (99)	287 (100)
	Co	423 (59)	530 (74)	573 (80)	685 (96)	707 (99)	714 (100)

Table 5 - Precision data for five batch extraction water analyses.

		Average Line Intensity (cps)	Standard Deviation (cps)	% Relative Standard Deviation
		Metal	Bi	140
	Pb	216	8	3.7
	Zn	290	5	1.7
	Cu	816	11	1.3
	Ni	773	23	3.0
	Co	717	12	1.7

minutes for each sample. All parameters were kept constant to determine the total precision of the preconcentration procedure and XRF analysis of water samples.

Table 5 lists the average intensity, the standard deviation and the percent relative standard deviation (% s. d.) for the five analyses of each analyte. The % s. d. best represents the reproducibility for metal determinations. All metals have good reproducibility at 200 ug metal, with values from 1.3 to 3.7 % s. d. However, Zn, Cu and Co (1.3 to 1.7 % s. d.) are significantly more precise than Bi, Pb and Ni (3.0 to 3.7 % s. d.).

Standard Curves

Table 6 lists the analyte spectral line intensities for the batch extraction standard curves and the amount of metal ion used to prepare the standard solutions. The data from Table 6 determined standard curves of the form $C_n = (I - b)/m$, where I is the intensity, C is the metal mass, m is the slope of the standard curve and b is the background intensity. The least squares linear regression values, m and b, are given in Table 7 for each element's spectral line. Figures 6, 7 and 8 represent graphically the standard curves for the batch extraction.

Table 8 lists the analyte spectral line intensities for the column extraction, and Table 9 lists the resulting standard curve constants. Figure 9 illustrates the standard curves we obtained by the column extraction.

Table 6 - Analyte spectral line intensities for batch extraction standard curves.

		INTENSITY (cps)						
		ug of metal ion						
		10	20	50	70	100	150	200
Metal	Pb	11	15	37	60	90	140	182
	Cu	29	63	186	226	338	524	677
		ug of metal ion						
		3	6	15	21	30	45	60
Metal	Ni	9	19	51	70	104	157	211
	Co	11	20	49	68	95	154	194
		ug of metal ion						
		25	50	125	175	250	375	500
	Zn	35	67	170	245	345	501	668

Table 7 - Batch extraction standard curve constants
for $C_n = (I-b)/m$.

STANDARD CURVE CONSTANTS

	m (cps/ug)	b (cps)
Pb	0.93	-3.5
Zn	1.33	4.7
Cu	3.43	-2.1
Ni	3.55	-2.5
Co	3.28	0.2

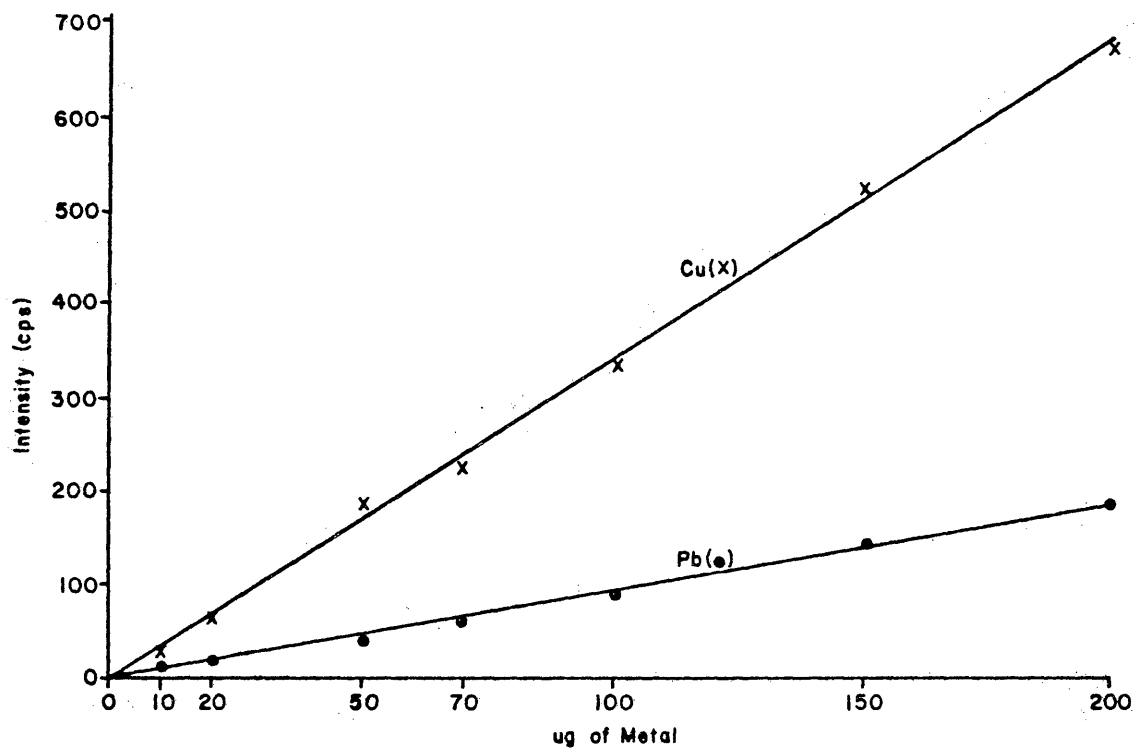


Figure 6. - Batch extraction standard curves for copper and lead.

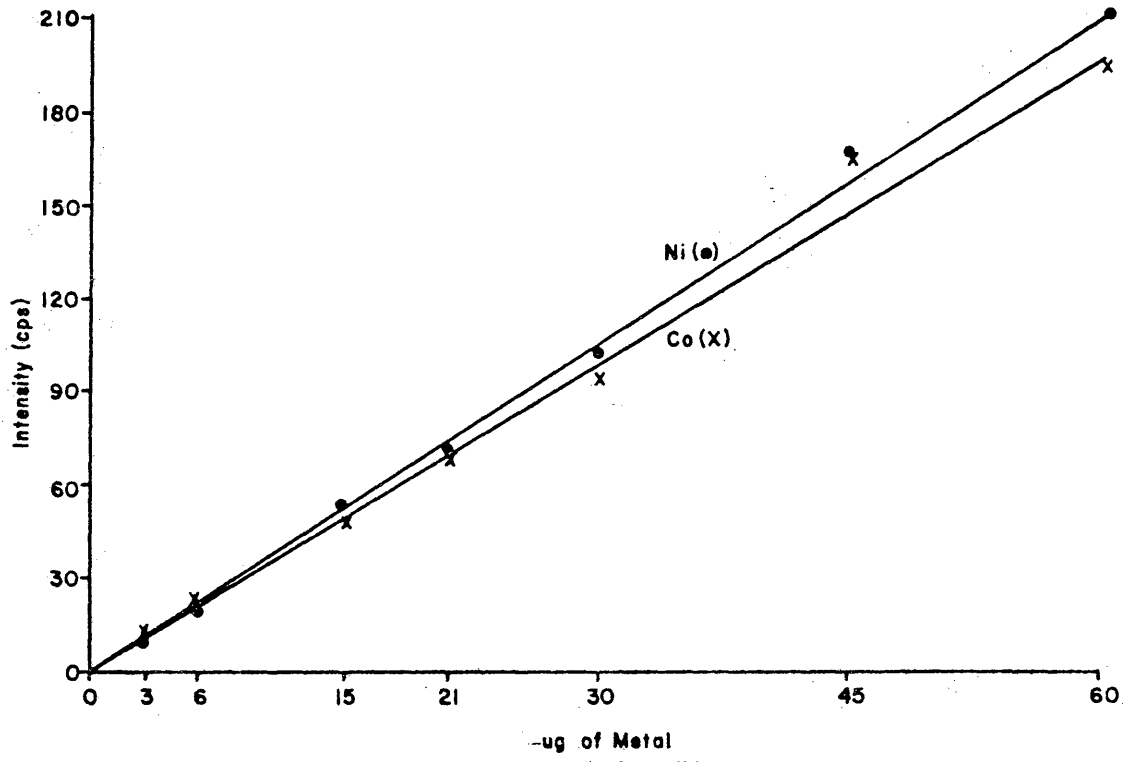


Figure 7 - Batch extraction standard curves for cobalt and nickel.

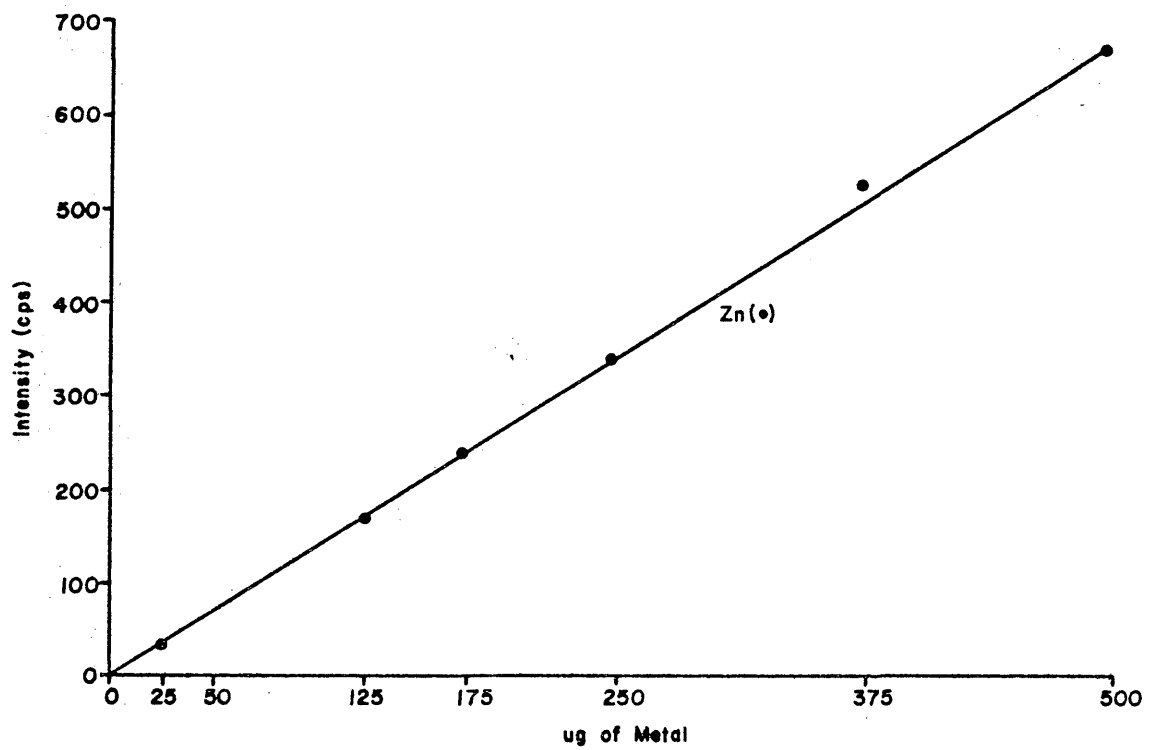


Figure 8 - Batch extraction standard curve for zinc.

Table 8 - Analyte spectral line intensities for column extraction standard curves.

Metal	INTENSITY (cps)				
	ug of metal ion				
	6.25	12.00	25.00	62.50	125.00
Bi	6	10	19	40	74
Pb	4	9	19	40	82
Zn	4	17	20	62	150
Cu	12	20	42	119	258
Ni	18	38	70	193	370
Co	11	39	71	189	352

Table 9 - Column extraction standard curve constants for $C_n = (I-b)/m$.

Metal	STANDARD CURVE CONSTANTS	
	m (cps/ug)	b (cps)
Bi	0.57	3.48
Pb	0.65	0.91
Zn	1.21	-5.25
Cu	2.09	6.57
Ni	2.98	-0.06
Co	2.85	0.56

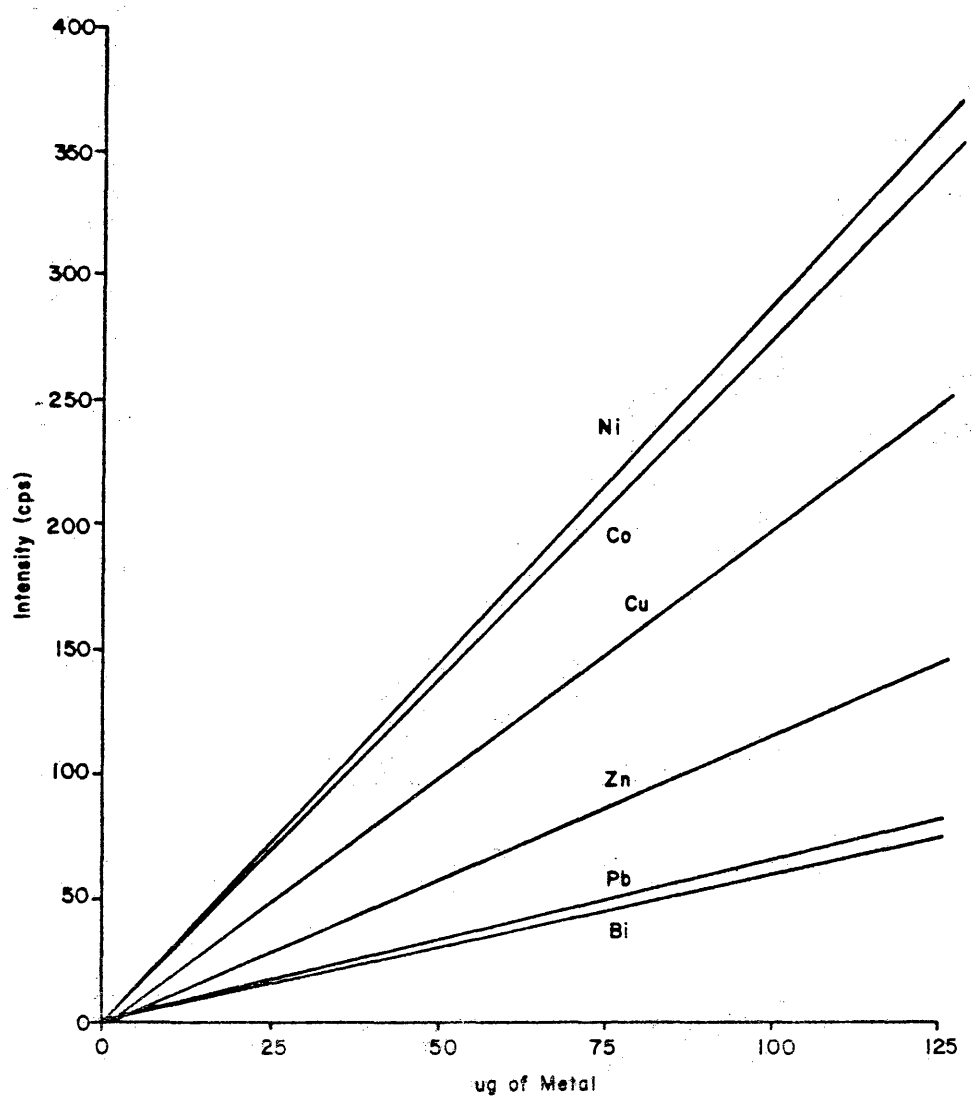


Figure 9 - Column extraction standard curves for bismuth, lead, zinc, copper, nickel and cobalt.

Detection Limits

Table 10 lists detection limits for five metals, calculated with equation 12. The background intensities (I_B) and sensitivities (m) were obtained from batch extraction standard curves. Included are the mass and concentration detection limits. The mass detection limit is the minimum amount of metal in the sample pellet that can be detected, and the concentration detection limit is the minimum detectable metal concentration in the original sample (of a given sample size). It is possible to make a qualitative analysis of the metal at values near the detection limit. To make a quantitative determination, the metal must be present in amounts of about three times the detection limit (Bertin, 1975). This value is the determination limit and is listed in parentheses in Table 10.

Table 11 lists trace metal concentrations found in several USGS rock standards (Flanagan, 1969), river water and sea water (Riley and Chester, 1976). These data allow comparison between detection limits and trace metal concentration in typical rock and water samples.

ROCK SAMPLE ANALYSIS

Preconcentration of Rock Standards

Tables 12 and 13 list the precision of four analyses of USGS andesite rock (AGV-1). Table 12 lists the metal concentrations

Table 10 - Mass detection limits calculated from $C_{DL} = (3/m)(I_B/T)^{0.5}$:
 T = 100 seconds. Concentration detection limits calculated
 for two sample sizes; determination limits given
 in parentheses.

DETECTION LIMITS

Metal	m (cps/ug)	I_B (cps)	Mass (C_D)		Concentration			
			Pellet (ug)		10 g Sample (ppm)	1 liter Sample (ppb)		
Pb	0.93	83	2.9	(8.7)	0.29	(0.87)	2.9	(8.7)
Zn	1.33	24	1.0	(3.0)	0.10	(0.30)	1.0	(3.0)
Cu	3.43	63	0.7	(2.1)	0.07	(0.21)	0.7	(2.1)
Ni	3.55	44	0.6	(1.8)	0.06	(0.18)	0.6	(1.8)
Co	3.28	41	0.6	(1.8)	0.06	(0.18)	0.6	(1.8)

Table 11 - Typical trace metal concentrations in rocks and natural waters.

		CONCENTRATION (ppm)*				
		Metal				
Material		Pb	Zn	Cu	Ni	Co
	Granite (G-2)	28.7	74.9	10.7	6.4	4.9
	Granodiorite (GSP-1)	52.4	143	35.2	10.7	7.5
	Andesite (AGV-1)	35.4	112	63.7	17.8	15.5
	Basalt (BCR-1)	18.0	13.2	22.4	15.0	35.5
	Peridotite (PCC-1)	13.3	53	10.4	2430	112
	River Water**	3	10	5	0.3	0.2
	Sea Water	0.03	5	1	2	0.8

* Water concentrations in ppb.

**World wide average.

obtained using standard curves to convert analyte line intensity to concentration, with the spectral line intensities in parentheses for each analyte. Table 13 lists the average concentration from the four analyses, their standard deviations, and the percent relative standard deviations. Tables 14 - 17 list the data from the analyses of four different USGS rock standards. The tables include the analyte line intensities, the metal concentrations obtained from standard curves, the accepted metal concentration values, and the concentration ranges (Flanagan, 1969). Comparing the determinations with the accepted values determine the accuracy of the preconcentration procedure. The rock standards analyzed include andesite (AGV-1), basalt (BCR-1), granodiorite (GSP-1) and peridotite (PCC-1). The andesite analyte intensities are an average of the four individual determinations listed in Table 12. The intensities for the other rocks are from one analysis. The trace metals were preconcentrated from one gram of rock sample.

Effect of Calcium

Table 18 lists the analyte spectral line intensities for samples containing calcium. The measurements were obtained from the preconcentration of solutions that contained 200 ug of each analyte and various amounts of calcium. The amount of calcium is reported as percent CaO, based on a one gram sample size. The line intensities reflect the effect of calcium on the preconcentration of metal ions in

Table 12 - Analyte determinations of andesite (AGV-1). One gram sample size. Analyte line intensities (cps) are in parentheses.

		CONCENTRATION (ppm)				
		Metal				
		Pb	Zn	Cu	Ni	Co
Sample	1	17 (12)	99 (136)	68 (230)	20 (68)	11 (35)
	2	12 (8)	95 (131)	59 (199)	19 (65)	12 (39)
	3	11 (7)	88 (121)	66 (223)	22 (76)	11 (35)
	4	17 (12)	101 (139)	64 (217)	20 (67)	12 (38)

Table 13 - Precision of four andesite (AGV-1) determinations.

		Average Concentration (ppm)	Standard Deviation (ppm)	% Relative Standard Deviation
Metal	Pb	14	3.2	22.4
	Zn	96	5.7	5.9
	Cu	64	3.9	6.1
	Ni	20	1.3	6.4
	Co	12	0.6	5.2

Table 14 - Accuracy of andesite (AGV-1) determinations. One gram sample size.

	Intensity* (cps)	Concentration (ppm)	USGS Mean (ppm)	USGS Range (ppm)
Pb	10	15	35.4	18-48
Zn	132	96	112	64-304
Cu	217	64	63.7	52-83
Ni	69	20	17.8	11-27
Co	37	11	15.5	10-33

* Average from four determinations.
See Table 12 for individual determinations.

Table 15 - Accuracy of basalt (BCR-1) determinations. One gram sample size.

	Intensity (cps)	Concentration (ppm)	USGS Mean (ppm)	USGS Range (ppm)
Pb	6	10	18.0	5-35
Zn	183	134	132	94-278
Cu	66	20	22.4	7-33
Ni	76	22	15.0	8-30
Co	105	32	35.5	29-60

Table 16 - Accuracy of granodiorite (GSP-1) determinations. One gram sample size.

	Intensity (cps)	Concentration (ppm)	USGS Mean (ppm)	USGS Range (ppm)
Metal Pb	12	17	52.4	14-80
Zn	144	105	143	54-340
Cu	132	39	35.2	15-54
Ni	38	11	10.7	3-25
Co	18	5	7.5	3-22

Table 17 - Accuracy of peridotite (PCC-1) determinations. One gram sample size.

	Intensity (cps)	Concentration (ppm)	USGS Mean (ppm)	USGS Range (ppm)
Metal Pb	8	12	13.3	*
Zn	45	30	53	24-100
Cu	39	12	10.4	5-16
Ni	3445	971	2430	1750-3400
Co	215	65	112	80-300

* Not available

rocks. The zero percent CaO sample shows the line intensities for samples containing no calcium. All other samples show the effect progressively increasing amounts of calcium has on the analyte line intensities. The line intensities are proportional to the amount of analyte extracted by the glass beads. Figure 10 shows the effect of calcium on metal ion extraction by plotting the data in Table 18 as intensity versus percent CaO. Figure 10 shows the analyte line intensities decreasing with increasing calcium concentrations. The intensity decrease is very pronounced for samples containing more than 15% CaO but less significant for samples containing 15% CaO or less.

A least squares linear regression analysis of the data for samples containing zero to 15% CaO in Table 18, eliminates the variations due to imprecision. The lines calculated from the linear regression are plotted in Figure 11. The constants that define the lines (I_0 and m) are also given in Figure 11. I_0 is the y-intercept of the line and m is the slope. I_0 indicates the analyte line intensity for zero percent CaO and m indicates the intensity decrease rate as a function of percent of CaO.

Calcium interference decreases the line intensity of the analyte lines, the decrease resulting in low metal determinations for rock analysis. The degree to which the determinations are lowered is dependent on the CaO concentration in the sample. Calculating the percent concentration decrease (D) for each 1% CaO present in the

sample by

$$D = (m/I_0) \times 100, \quad (13)$$

the values for m and I_0 were obtained from Figure 11, for each analyte. The constants and calculated D values are listed for each analyte in Table 19. D represents the percent change in analyte line intensity for each 1% of CaO that is present in a one gram sample.

The analyte line intensities for samples containing zero to 15% CaO (Table 18) were statistically analyzed to determine if varying amounts of calcium affect analytical precision. Table 20 lists the results of this precision study.

Table 18 - Analyte line intensity of samples containing various amounts of calcium. The % CaO is calculated for a one gram sample size. 200 ug of each metal.

		INTENSITY (cps)						
		% CaO						
		0	5	10	15	20	25	30
Metal	Bi	124	127	120	112	19	8	16
	Pb	223	247	219	209	216	191	62
	Zn	295	306	274	269	256	224	172
	Cu	797	751	737	774	642	591	455
	Ni	779	703	667	693	632	547	419
	Co	720	686	616	635	539	484	293

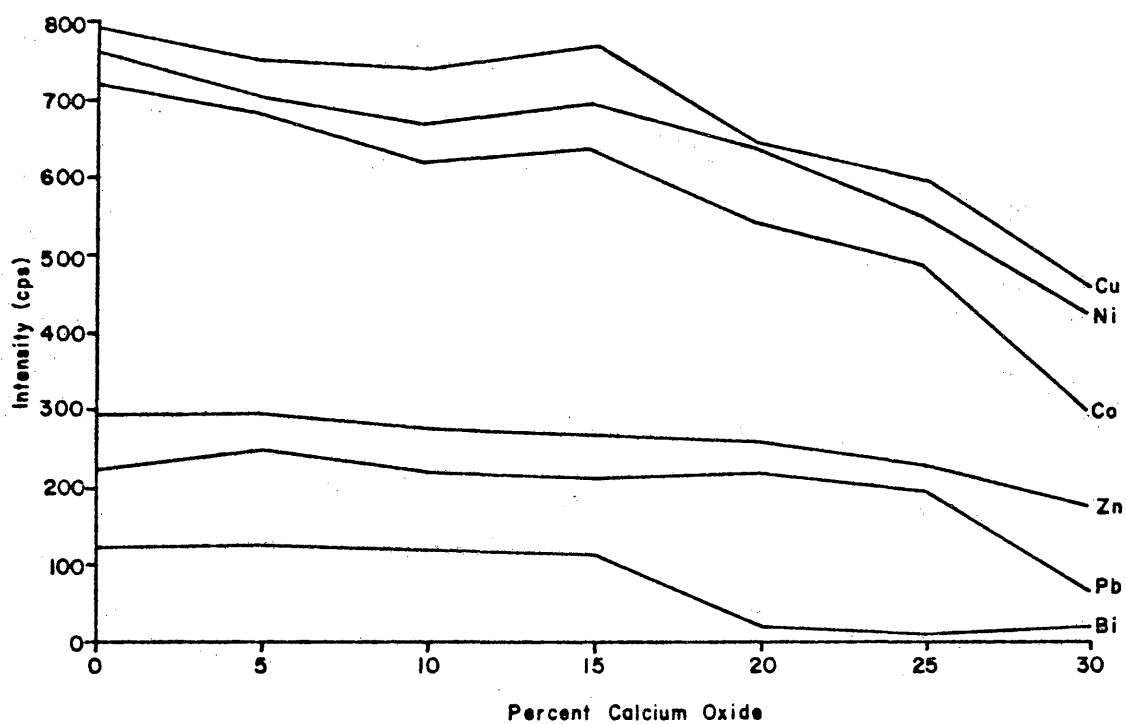


Figure 10 - Effect of calcium on analyte line intensity. Percent calcium calculated for a one gram sample. Two hundred micrograms of each metal.

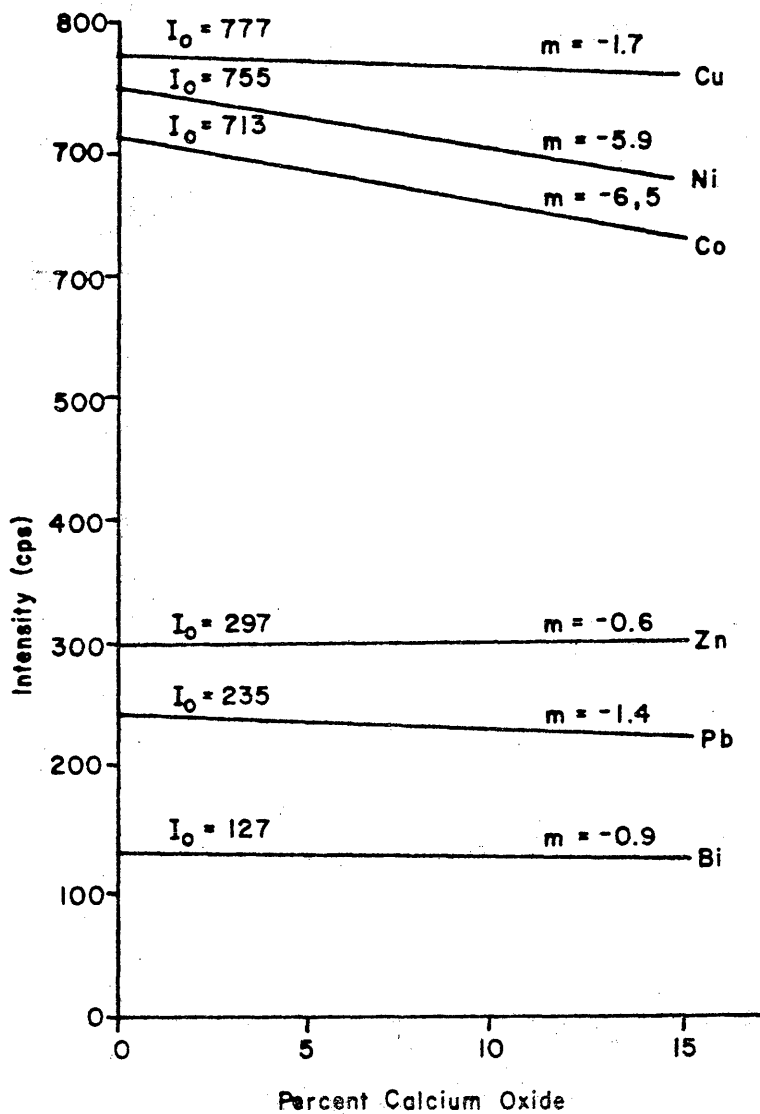


Figure 11 - Linear regression curves of analyte line intensity versus percent CaO.

Table 19 - Percent change in analyte line intensity (D), for each 1% CaO. Calculated for a one gram sample. $D = (m/I_0) \times 100$.

	m	I_0	D
Bi	-0.9	127	-0.7
Pb	-1.4	235	-0.6
Zn	-0.6	297	-0.2
Cu	-1.7	777	-0.2
Ni	-5.9	755	-0.8
Co	-6.5	713	-0.9

Table 20 - Precision of four analyses for samples containing zero to 15% CaO, calculated for one gram sample size.

	Average Intensity (cps)	Standard Deviation (cps)	% Relative Standard Deviation
Bi	121	6.5	5.4
Pb	225	16.1	7.2
Zn	286	17.5	6.1
Cu	765	26.4	3.5
Ni	711	48.1	6.8
Co	664	47.5	7.2

DISCUSSION

SAMPLE PELLETT PREPARATION

Comparative Study of Three Pellet Preparation Methods

The no-matrix pellet is superior to the pressed and fused pellets for preconcentrated trace metal analysis. The no-matrix method yields much higher analyte line intensities resulting in improved detection limits. The pressed and fused pellet procedures dilute the trace element concentrations by adding a flux or binder to the sample. The lithium tetraborate flux and the boric acid binder absorb primary and secondary radiation, attenuating the line intensities. The intensities of the lithium tetraborate pellet are almost one half as intense as the boric acid pellet. The pressed and fused pellets used the minimum amount of binder or flux to make useful sample pellets.

The pressed and fused pellet preparations were originally designed for the analysis of major, minor and the more concentrated trace elements in rock samples. Major or minor element analysis does not suffer significantly from sample pellet dilution, in fact dilution reduces the magnitude of matrix corrections. However, sample pellet dilution certainly places many trace element concentrations near, or below the detection limit, making some determinations impossible and reducing the precision for others. Sample pellet dilution reduces the advantage gained from preconcentration.

The no-matrix pellet preparation has advantages other than high analyte intensities, it is fast and convenient, and avoids the introduction of impurities from grinding the sample or from additional pellet matrix. However, there is contamination resulting from the sample holder not introduced by the fused or pressed sample holders.

Qualitative analysis of blank samples revealed large copper peaks originating from the sample holder. The sample holder is made from an Al-Cu alloy. A high purity aluminum (99.999% pure) sheet was placed on the analyzing surface of the sample holder to reduce the copper contamination. Aluminum was chosen because we had no interest in analyzing that element. A hole cut in the aluminum sheet exposed the sample to the x-ray beam. This precaution considerably reduced but did not eliminate the copper contamination. The rest of the copper contamination originated from the support disk, directly behind the glass beads. A high purity metal disk (the radiation enhancer) was placed between the support disk and the glass beads to eliminate this source of contamination. The combination of the secondary support disk and aluminum sheet satisfactorily reduced sample holder contamination by copper. The aluminum sheet and secondary support disk was used for the analyses listed in Table 1.

It might be better to substitute polyethylene for the Al-Cu alloy used in the sample holder. Polyethylene does not have the major impurities of the Al-Cu alloy, the high purity aluminum shield may not be necessary and polyethylene lasts well in the x-ray beam. Eliminating the aluminum shield will make the holder less complex,

less expensive and reduce contamination. Reducing contamination will improve the signal-to-noise ratio and improve detection limits.

Sample Holder Radiation Enhancer

A molybdenum radiation enhancer gave a significant advantage in analyte line intensities as compared to the aluminum enhancer. The aluminum enhancer acted as the control for no radiation enhancement. Each analyte element exhibited an increase in its emission line intensity using the molybdenum radiation enhancer. The fluorescence of the molybdenum enhancer increases x-ray flux striking the sample. The increased radiation excites a higher proportion of the analyte elements at any given moment, resulting in greater analyte line intensities, hence greater precision and accuracy.

If radiation enhancement were the only effect, we would expect the percent intensity improvement to be proportional to the excitation potential of the analyte spectral line. The analyte spectral line with an excitation potential closest to (but not below) the energy of the Mo K alpha should increase the most. The Bi L alpha should exhibit the strongest increase in intensity, while the Co K alpha intensity should increase the least. We do not observe this relationship between the excitation potential and line intensity increase. Deviations from this relationship are due to enhancer contamination.

Contamination accounts for an increase for some analyte line intensities with the molybdenum enhancer. The aluminum backing

plate is 99.999% pure aluminum contributing very little contamination. The molybdenum enhancer is only 99.95% pure. The manufacturer lists copper as a major contaminant of the molybdenum, with Pb, Ni and Co as minor contaminants. The Bi and Zn line intensities represent the true increase due to the molybdenum radiation enhancer, since they are not contaminants.

The enhancer contamination is not high enough to affect the accuracy of the analysis significantly. The contamination raises the calculated value of b (background intensity) in the standard line equation (equation 10). Subtracting b from the spectral line intensity (I) corrects for the contamination. Using purer molybdenum for the enhancer may improve analytical precision by reducing the variation in contamination from different enhancers.

Materials other than molybdenum may also serve as radiation enhancers. For example, a lead enhancer will improve the first row transition element line intensities more than a molybdenum enhancer. However, a lead determination will be impossible with a lead enhancer, and lead will not improve the bismuth line at all. Enhancers made from two different materials will allow a broader range of elements to benefit from the enhancer. The choice for enhancer material must be made on the elements to be determined and the element needing the most radiation enhancement.

Effect of Pellet Thickness

Figure 3 illustrates the relationship between line intensity and pellet mass. The Cu K alpha line intensity increases linearly to a pellet mass of 75 mg and then increases nonlinearly to a maximum at a 200 mg pellet mass. As the pellet mass increases, the mass of copper in the pellet increases proportionally. The greater the copper mass, the greater the Cu K alpha intensity. However, the relationship between intensity and pellet mass is not linear beyond a pellet mass of 75 mg. The line passes through a maximum and the slope of the line becomes negative.

We can explain this phenomenon in terms of pellet thickness, which is proportional to pellet mass. The gradual decrease in intensity with pellet thickness is due to primary and secondary x-ray absorption by the matrix. Absorption is minimal for very thin pellets and analyte intensity is essentially proportional to pellet thickness, up to a pellet mass of 75 mg. For thicker pellets, the attenuation of primary and secondary radiation increases with depth. The spectral line intensity continues to increase but at a lower rate. An x-ray emission, beyond a certain depth in the sample results in the absorption of the x-ray before it can escape the pellet. This thickness is the "infinite" or critical thickness of the pellet (Bertin, 1975). Infinite thickness varies with matrix and x-ray wavelength.

When the pellet equals infinite thickness, the rate of increase is expected to be zero. However, the rate becomes negative beyond

a sample mass of 200 mg. If the pellets exceed infinite thickness for molybdenum the radiation enhancer can not excite the metals in the pellet. Since the enhancer does not function, the analyte intensities decrease. The intensity is greater for a 200 mg pellet than for 250 mg, illustrating that infinite thickness is at a pellet mass of about 200 mg or greater.

A 200 mg pellet yields the highest intensity for the Cu K alpha line. Pellet thickness for maximum analyte line intensity will vary for other elements. Elements with a lower energy spectral line than copper will reach maximum intensity at a smaller pellet mass than for copper. Elements with a higher energy spectral line than copper will reach maximum intensity at a larger pellet mass. The Cu K alpha was chosen for this experiment because it is intermediate in energy of the elements studied.

Although a pellet mass of 200 mg yields the highest Cu K alpha line intensity, it is not the optimum pellet mass. Since all the pellets studied had the same copper concentration but different pellet masses, the copper mass is larger in the heavier pellets, thus requiring larger original samples for equivalent intensities. For a given copper mass (or sample size), the 75 mg pellet is most efficient. A 200 mg pellet containing 200 ug of copper has a Cu K alpha line intensity of 483 cps. Calculations show that a 75 mg pellet with 200 ug of copper will have a 896 cps Cu K alpha line intensity, or an improvement of 86% over the 200 mg pellet. For analyses requiring maximum

sensitivity, 75 mg pellets should be used. For reasons of consistency, 100 mg pellets were used in the remainder of this investigation. However, 75 mg pellets increase intensities about 16% over the 100 mg pellets.

CONDITIONS AFFECTING METAL ION EXTRACTION

Extraction as a Function of pH

Figure 4 gives pH extraction curves for five minutes mixing, representing an unequilibrated extraction. The pH with the maximum analyte line intensity is the pH giving the most rapid extraction rate for the cation. Each cation has a single pH where extraction is fastest, but on the average, multielemental extraction rates are fastest at a pH ranging from 8 to 10. Figure 5 gives pH extraction curves for forty minute mixing, representing an equilibrated extraction. The pH with the maximum analyte line intensity is the pH giving the most complete cation extraction, and each cation has a single pH where the extraction is most complete. Multielemental extractions are most complete at a solution pH ranging from 8 to 9. The solution pH of 9 has a slightly higher percent average intensity (98%) than pH 8 (95%), but the difference is probably not significant, and may be due to analytical imprecision. The pH range yielding the fastest extraction rates (8 to 10) is similar to the pH range giving the most complete extraction (8 to 9). Multielemental extractions

should take place in solution pH between 8 and 9 to assure a complete and rapid cation extraction.

Irregularities in the extraction curves, particularly the extraction of Bi, Pb and Cu at low pH, are probably a result of two types of metal-ligand complexes that are pH dependent. These pH curves were compared with curves of Leyden and Luttrell (1975b), who used silylated silica gel rather than glass beads. A comparison of these data to Leyden and Luttrell's curves show little significant differences. Leyden and Luttrell give extraction curves for all elements in this study except bismuth. They also included pH extraction curves for Mn, Hg, Eu, Fe, Ag, Cd and Cr which were not studied in this research.

Extraction as a Function of Time

The effect of mixing time on batch extraction was determined for Pb, Zn and Co (Table 4). All metals reached 99% of their maximum intensity with ten minutes of mixing. In a similar experiment nickel reached 98% maximum intensity with ten minutes mixing, bismuth 97% and copper 100%. A ten minute mixing time appears to be adequate for multielemental extractions at pH 8.

Leyden and Luttrell (1975b) performed experiments to determine the relationship between the percent maximum intensity of an analyte line and the percent analyte metal extracted from solution. They analyzed solutions containing metal ions by atomic absorption

spectrometry, before and after extractions with silylated substrates. They calculated distribution coefficients that represented the amount of metal extracted onto the substrate from the solution. These coefficients indicate the extractions are quantitative (over 99% extracted) at mixing times yielding the highest analyte line intensities. The percent of the maximum intensity for an analyte indicates the percent metal extracted from solution.

The mixing time data are only valid for an extraction in a solution of pH eight. The solution pH controls the extraction rate, so a solution pH that yields fast extraction rates for all elements was used. The data are also only valid for batch type extractions. Leyden and Luttrell (1976a) investigated extraction rates for column type extractions, calculating extraction rates as solution flow rates (ml/minute) through the column. Their investigation showed flow rates up to 70 ml per minute quantitatively extract ions from solution.

EXTRACTION OF METAL IONS FROM WATER SOLUTIONS

Precision Study

The data of Table 5 reflect the total precision for the extraction of 200 ug of each metal ion from solution, by the batch extraction procedure, and XRF analysis. A metal mass of 200 ug is a reasonable quantity for a rock of sample size between 1 and 10 g. The results of the precision study show adequate reproducibility for samples in this concentration range.

Zn, Cu and Co are about twice as precise as Bi, Pb and Ni. Bi and Pb had the lowest analyte line intensities and imprecision will result from greater count rate variation. Nickel had the lowest extraction rate of all metals at pH eight (Table 3). The poor nickel extraction at this pH may contribute to the imprecision.

Standard Curves

Two sets of standard curves were made by measuring analyte line intensities from standard solutions. The curves were linear, confirming the theoretical linear relationship between analyte line intensity and trace element concentration in a constant matrix.

For samples with metal concentrations in the ppm range, the batch extraction procedure was used. Rock determinations usually fall in the ppm range. When the batch extraction standard curves were made, we chose metal concentration ranges in the standard solutions similar to concentrations we expected to find in rock samples, with concentration ranges exceeding an order of magnitude.

For metal concentrations in the ppb range, a column extraction is used. Water analyses usually fall in the ppb range. Since natural waters usually have very low metal concentrations, the sample must be large to detect the metal. Convenience in preparing a large water sample (100 ml or greater) prompted the use of a column extraction procedure. The standard curves of the column extractions cover the same concentration range for each element, because of

difficulty in predicting which metals will have high or low concentrations for natural water samples. The slopes (m) of the column extraction curves differ from the slopes of the batch extraction curves, primarily because of different x-ray instrument conditions.

Trace metals preconcentrated onto the silylated glass beads yield linear standard curves, at low concentrations. The bead capacity limits the linear range of the curves. Investigations show that standard curves remain linear up to 60% of the bead capacity (Leyden and Luttrell, 1976a). Calculations show bead capacity to be about 1.0 meq/g (Leyden and Luttrell, 1975b). Qualitative experiments support these values. The bead capacity is substantially lower than many ion exchange resins currently in use. Fortunately, ethylene diamine functional groups have little or no affinity for group I and II elements (Leyden and Luttrell, 1976a and Dingman et al., 1972), and can effectively preconcentrate trace metals in the presence of large amounts of these elements. This is very important for preconcentrating trace elements in natural materials, where large amounts of group I and II elements are often present.

It may be more efficient to eliminate the batch extraction procedure, and use the column extraction procedure for all types of analyses. The exclusive use of column extractions will eliminate the need for batch extraction equipment, and standardize the extraction procedure for water and rock analyses. The use of the column extraction procedure will become easier if control rate solution pumps are used to control the column flow rate.

Leyden et al. (1976a and 1976b) investigates water analysis by this preconcentration procedure extensively. We do not further pursue water analysis, except for the calculation of detection limits.

Detection Limits

Table 10 lists detection and determination limits calculated for metal mass in the pellet and metal concentration in given sample sizes. The concentration detection limits for ten gram samples are for rock analysis, which is about the largest amount of rock sample useful for preconcentration. Preconcentrating trace metals from ten grams of rock sample onto 100 mg of silylated glass beads represents a concentration factor of 100X, or one hundred times more concentrated than in the original sample.

The determination limits for ten gram samples should be adequate for most rock determinations. We list the metal concentration found in six USGS rock standards in Table 11. All of the listed trace metals in that broad suite of rock types are above the determination limits. In fact, a 10X concentration factor (one gram sample) is adequate for trace metal determination in those six rock types. However, a larger sample may improve precision by providing a more representative sample and improving the statistical x-ray count variation.

The concentration detection limits for the 1000 g (one liter) sample, represents a concentration factor of 10,000X. The

determination limits indicate the preconcentration procedure may be useful for many types of natural water analyses, particularly where the trace metal concentration may be enriched, such as mine or waste waters. Table 11 lists trace metal concentrations in sea water. Only zinc and possibly copper are above the determination limits, and lead is above the detection limit. Cobalt and nickel are below the detectable range.

It is possible to improve the detection limits by using a larger sample. Dingman, et al. (1972) used 20 liters of synthetic sea water for trace metal preconcentration onto ion exchange resin. A 20 liter sample will improve our determination limits enough to analyze the five trace metals listed in Table 11 for sea water. Using a more efficient radiation enhancer can improve specific trace metal detection limits. Using 75 mg rather than 100 mg pellets improves analyte line intensity, therefore improves detection limits. Changes in the x-ray spectrometer also improve detection limits. The measurements for the detection limits were made on a XRF spectrometer using a full-wave x-ray generator. A full-wave generator produces high energy x-rays only a fraction of the operating time. The metals in this study require excitation by high energy x-rays, therefore a full-wave generator gives poorer detection limits than a constant potential x-ray generator, which produces high energy x-rays 100% of the time. Near the end of this investigation, we ran analyses to determine how much the detection limits improve with a constant

potential generator. The detection limits improved 20% for Ni and Co, 25% for Zn, 71% for Pb and 75% for copper. Increasing the power of the generator will also improve heavy trace metal detection limits (but shorten x-ray tube life). We used a chromium anode x-ray tube for all analyses in this investigation. A Ag, W or Mo tube will improve heavy trace metal detection limits considerably.

Detection limits were calculated using a constant potential x-ray generator, 75 mg pellets and a one liter sample:

Pb - 1.5 ppb

Zn - 0.7 ppb

Cu - 0.4 ppb

Ni - 0.4 ppb

Co - 0.4 ppb

These improvements are easily made using equipment in this laboratory. Using a heavy metal anode x-ray tube operated at high power will easily reduce these detection limits by one-half. Increasing water sample size will reduce the detection limits proportional to the increase in sample size.

ROCK SAMPLE ANALYSIS

Preconcentration of Rock Standards

Table 13 list the results of the precision study. Co, Cu, Ni, and Zn have a percent relative standard deviation (% s. d.) ranging

from 5.2 to 6.4% s. d. The previous precision study of water solutions gave values ranging from 1.3 to 3.0% s. d. for the same elements. The rock preparation procedure introduces an estimated 3 to 5% s. d. of the entire preconcentration procedure, for these four elements. The precision (22.4% s. d.) of the Pb analysis is much poorer than for other elements.

There are many possible reasons why rock analysis is less precise than water analysis. The rock preparation procedure requires much more sample preparation than water analysis. Sample loss or contamination is much more likely for rock analysis. Rock samples are not as homogeneous as water samples and sampling error can result. Inhomogeneity can be greater for trace elements than major elements in rocks. Selecting a nonrepresentative sample constitutes one of the largest single sources of experimental error for trace element analysis in rocks (Ingamells and Switzer, 1973). Most of a given trace element may be present in a relatively small number of usually heavier grains in the powdered sample. Using a larger sample improves precision by giving a more representative sample, and also increases the precision of the x-ray counting statistics by increasing the analyte line intensity. In rock preparation, the adsorption and elution procedures require a constant resin column flow rate. With our equipment flow rate control was difficult. We believe a significant improvement in precision will result if we control the column flow rates closely. With the type of resin column

we used, flow rates can vary by more than 100%. The use of control rate peristaltic solution pumps should eliminate this variation, as well as reducing the time spent on sample preparation.

Tables 14 - 17 give the results of the accuracy studies. Of 20 analyte determinations, three values are outside (below) the USGS reported range. One of the low values is for lead in the AGV-1 standard. The other two low values are Ni and Co in the PCC-1 standard. The PCC-1 standard is peridotite containing over 43% MgO. We previously analyzed nonstandard rocks that contained similar amounts of CaO. These samples also yielded erratic trace metal determinations. Large quantities of Mg or Ca interfere with the preconcentration of trace metals. We pursue this problem further in the next section.

The precision and accuracy of the lead values are generally much poorer than the other metals. The lead values do not have erratically high and low values, but are consistently below the USGS reported mean. The problem appears to be limited to preconcentration of lead from rock samples. We preconcentrated the trace metals from the standard solutions by the same method we use for rock samples, i. e., we use the iron removal step. The analyses of the standard solutions are precise and accurate for all elements, including lead. We feel the problem of the lead determinations in rocks is a result of poor rock digestion technique. Some of the rock is not in solution after we add the 1N HF, prior to the ion exchange resin

extraction. The residue is discarded with any lead it may contain. Some of the other metal ions may be trapped in the residue, contributing to the imprecision of all metal determinations. Lead and nickel may also be in sulfides not easily digested by the method we used. Metals in the sulfides may yield low values. The use of a digestion procedure that assures complete dissolution of the rock should improve the accuracy and precision for all trace metal determinations. It is doubtful that a single digestion procedure will be ideal for all rock samples. The digestion procedure used was for total rock analysis. Other digestions may be useful for analysis of plant materials, partial extractions, etc. Partial extraction, e. g. with cold extractable HCl, should suffer little from the possibility of excess calcium or magnesium.

For the analysis of rock standards, we find the preconcentration procedure usually works well. The precision is acceptable for Cu, Ni, Co and Zn. The precision may improve with rigorous control of column flow rates. Most of the calculated values for Cu, Ni, Co and Zn are near the USGS means. All these elements are within the USGS range with the exception of elements from the PCC-1 standard. The method does not work well for lead, or for rocks containing large amounts of Ca and Mg. The next section discusses how much calcium may be present in a sample and still yield acceptable trace metal determinations.

Effect of Calcium

Experiments indicate that large amounts of calcium (and magnesium) in rocks interfere with the preconcentration of trace metals. This experiment established the range of CaO concentration, where trace metal preconcentration is practical. Figure 10 illustrates the effect is probably due to the loading of these elements on the ion exchange resin. Calcium and magnesium compete for available ion exchange sites with the trace metals. An excess of calcium or magnesium results in a nonquantitative extraction of trace metals onto the resin. The use of a larger quantity of resin may reduce the interference by calcium and magnesium.

Table 20 lists the analytical precision for samples containing zero to 15% CaO. The precision is about the same as for the andesite determinations (Table 13). Imprecision resulting from variable amounts of calcium does not appear to be significant.

CONCLUSIONS

This preconcentration procedure yields encouraging results for trace metal determinations. Preconcentration has several advantages over direct sample analysis. The procedure increases trace element concentration to improve detection limits. Trace elements in water samples analyze as a solid, avoiding the problem associated with liquid XRF analysis. Matrix effect calculations are not necessary for elemental determinations. Those advantages are common to most preconcentration procedures.

This preconcentration procedure has advantages not found in other similar procedures. This method preconcentrates several trace elements simultaneously, taking advantage of the multielemental determinations possible with XRF analysis. The method can also preconcentrate trace metals from both rock and water samples. The sample pellet preparation technique increases analyte line intensity and improves detection limits. These were the basic research objectives at the beginning of this investigation.

The procedure has met the original objectives, and specific aspects of the procedure can be improved to yield better results. The investigation has resulted in several conclusions in specific areas of the research, and some suggestions on improvement:

- 1) The no-matrix pellet increases analyte line intensities over fused or pressed pellets. By avoiding additional matrix in the pellet,

excessive secondary x-ray absorption is eliminated, and detection limits are improved. Using a polyethylene sample holder may result in a simpler sample holder design and reduce contamination.

2) The molybdenum radiation enhancer increases analyte line intensities for the elements studied. Other materials can be used for the enhancer to improve specific analyte lines. Enhancers made from two materials may improve intensities for multielemental determination covering a broad range of x-ray energies.

3) A sample pellet mass of 75 mg yields the highest analyte line intensity for a given metal mass in the pellet. A pellet mass over 200 mg reduces the effectiveness of the molybdenum enhancer.

4) Each element has a unique solution pH where extraction is fastest and most complete. For multielemental extractions of metals studied, the extraction is most efficient with a solution pH from 8 to 9.

5) For the metals studied, the extraction is complete after ten minutes of mixing, by the batch extraction procedure. The extraction procedure may be simplified by using only the column extraction procedure for rock and water analysis. The column extraction procedure should give better results if peristaltic pumps control the solution flow rate through the column.

6) The precision of trace metal determinations from water solutions is good: 1.3 to 3.7% relative standard deviation with 200 ug metal. Other investigators have proved the value of this procedure for trace element determinations in natural waters.

- 7) Linear standard curves replace the matrix effect calculations usually required for XRF analysis.
- 8) The silylated glass beads have adequate capacity for trace element pre-concentration from natural materials, because ethylenediamine selects against group I and II elements, which often occur in high concentrations in natural materials. Other silane compounds with different functional groups may be used for pre-concentration (Leyden and Luttrell, 1975b and 1976a).
- 9) The concentration detection limits range from 0.06 to 0.29 ppm for rock samples (ten gram sample), and from 0.6 to 2.9 ppb for water samples (one liter sample). Further improvements can be made by using larger samples, 75 mg pellets, more efficient radiation enhancer, constant potential x-ray generator operated at higher power, and a heavy metal anode x-ray tube.
- 10) The precision and accuracy of Co, Ni, Cu and Zn determinations were generally adequate for rock analysis. Lead determinations were imprecise and yielded low value, probably due to poor rock digestion. Solution pumps controlling the flow rate through the resin columns should improve precision, and simplify the procedure.
- 11) Calcium and magnesium interfere with the pre-concentration procedure. Rock samples containing over 15% CaO or MgO may yield low trace metal determinations. Increased amounts of cation exchange resin in the column may reduce this problem. Rocks containing less than 15% CaO or MgO suffer interference to a small

degree, and the error can be corrected. Changing the CaO sample concentration from zero to 15% CaO, does not significantly affect analytical precision.

12) Multielemental determinations from water solutions are not limited to Bi, Co, Cu, Ni, Pb and Zn. Other elements can also be determined by this method. Leyden and Luttrell (1975b) preconcentrated Hg, Eu, Mn, Fe, Ag, Cd and Cr from water solutions by a similar procedure. Leyden et al. (1976b) also preconcentrated the oxyanions of As, Mn, Cr, Se, Mo, W and V from water solutions.

13) The variety of elements preconcentratable from rocks is more limited than for water solutions. Elements must adsorb onto the ion exchange resin (from dilute HF solution) as well as the glass beads, for rock analysis. There are several metals that are known to adsorb onto both the Dowex-50 cation exchange resin and the glass beads that we did not study, including Mn, Ag and Cd (Danielsson, 1965). Hg and Eu are also likely to adsorb onto both substrates, but no confirming data is available.

14) The utility of the method may be increased by using Dowex-1 anion exchange resin mixed with the Dowex-50 cation exchange resin. Dowex-1 adsorbs Mo, Nb, Sb, Sn, Ta, Ti, V, W and Zr, from dilute HF solution (Danielsson, 1965). Further research can confirm the possibility of preconcentrating these elements.

APPENDIX I

Silylation Reaction - Procedure

Appendix I describes the silylation reaction to prepare the glass beads for extractions. The reaction attaches an alkoxy silane compound, containing amino functional groups, onto controlled-pore glass beads (Electro-Nucleonics Inc., #CPG 240). The glass beads are 200/400 mesh, have a mean pore diameter of 259 Å with a pore size distribution of $\pm 8.2\%$, a pore volume of 1.31 cc/g, and a surface area of 118 m²/g. The alkoxy silane compound is N-aminoethylaminopropyltrimethoxysilane, or Dow-Corning Z-6020 (PCR Research Chemicals, Inc., #34070-3).

Stir ten grams of glass beads for four hours in 200 ml of 1:1 HNO₃. Collect the beads in a Buchner filter funnel. Use 100 ml of deionized water to rinse the HNO₃ from the beads. Prepare a solution of three drops of acetic acid and ten ml of the alkoxy silane in 90 ml of deionized water. Add the glass beads to the solution, and stir the mixture for one hour at 80° C. Pass the solution through a filter to recover the beads, and rinse the excess solution from the beads with 100 ml of deionized water. Wash polymerized silane compound from the beads with 100 ml of toluene. Fifty ml of isopropyl alcohol wash removes excess toluene. Cure the beads at 80° C for eight hours. The silylated glass beads are stable, and can be stored at room temperature.

APPENDIX II

Iron Removal from Rock Samples

This procedure is only for rock samples, and it serves two purposes. First, it removes elements that may interfere with the extraction procedures (Appendix III). Second, it places the metals of interest into a water solution. The extraction procedure requires the metals to be in a water solution.

Prepare a column for the ion exchange resin, and associated apparatus, as shown in Figure 12 and 13. The three inch long column is made from 1/4 inch i. d. polyethylene tubing. A 1/4 inch piece of the tubing is placed inside the column, to support the material inside the column. Fifty mg of teflon wool (Supelco, Inc. #2-0597) rests on the support and prevents resin from washing out of the column. The column attaches to the stem of a five cm plastic Buchner filter funnel (Sargent-Welch, #S-35620-C), which inserts through a single hole rubber stopper. Remove the funnel reservoir from the funnel stem, and insert the apparatus into a 500 ml plastic filtering flask (Sargent-Welch, #S-34380-E). A rubber hose connects the filtering flask to a vacuum source. Place three grams of Dowex-50W ion exchange resin (Sigma Chemical Co., #50X8-200) into the funnel stem. The resin is 100/200 mesh, H⁺ form, 8% cross linked cation exchange resin. Wash the resin into the column with deionized water,

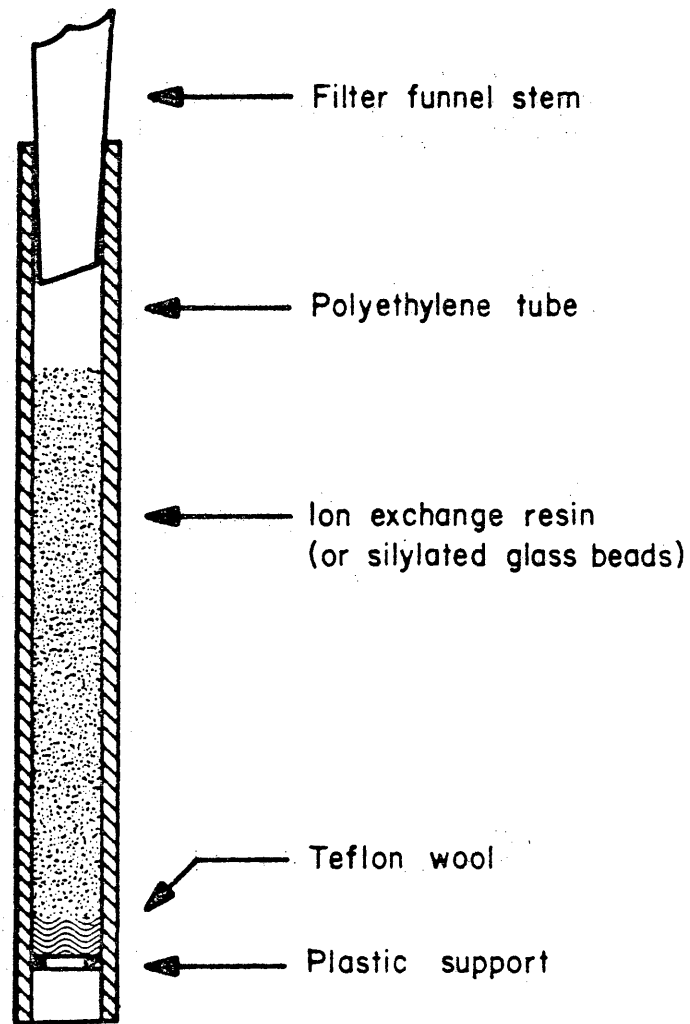


Figure 12 - Ion-exchange resin column for iron removal (cross-section). The column is also used for the glass bead column extraction by replacing the resin with silylated glass beads.

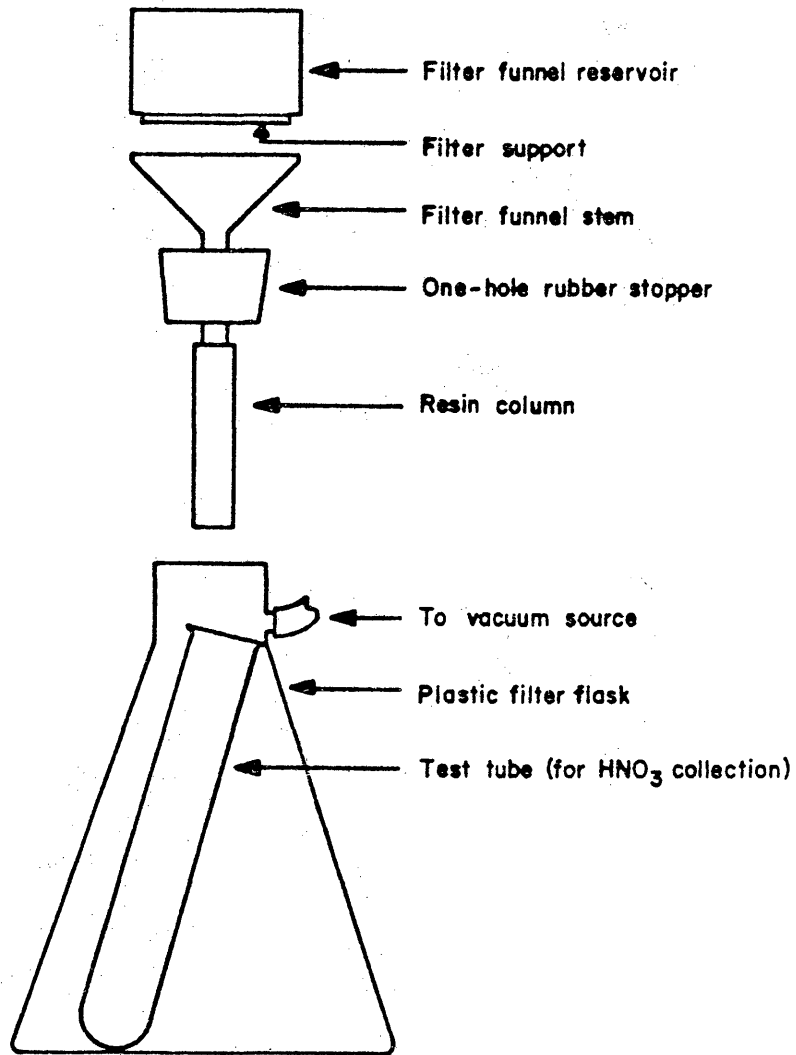


Figure 13 - Ion-exchange column apparatus for iron removal.

and insert the funnel reservoir onto the funnel stem. This completes the construction of the apparatus required for the iron removal procedure. Several sets of apparatus can be made to prepare several rock samples simultaneously.

Begin sample digestion by powdering the rock sample in a ball mill. Heat sample in oven at 105°C for four hours and place in desiccator until weighing. Accurately weigh one to ten grams of sample and place in teflon beaker. For each gram of sample, add the following proportion of concentrated acids to digest the powder. Add two ml HNO_3 and five ml HClO_4 to sample. Warm mixture on hot plate for 30 minutes and allow to cool. Add 20 ml HF and replace beaker on hot plate, allowing the acids to slowly evaporate overnight. Add 100 ml 1N HF to the residue, regardless of original sample size, and stir for one hour.

The iron removal procedure uses the following amounts of acids, independent of original sample size. Place a five cm filter paper in the filter funnel, and apply a vacuum to the filtering flask. Pour the 1N HF solution, containing the rock sample, into the funnel reservoir and adjust the vacuum to achieve a flow rate through the column of two ml/minute. The resin adsorbs the metals of interest. After the solution passes through the column, wash any residue on the filter paper with small quantities of 1N HF, and allow the washings to pass through the column. Remove filter paper and residue from the funnel. Add 50 ml 1N HF to the funnel reservoir and allow the

acid to pass through the column. The acid washes excess iron from the resin. Discontinue vacuum and remove filtering funnel-column apparatus from the filtering flask. Discard the dilute HF solution, and place a large test tube in the filtering flask. Replace filtering funnel-column apparatus into the filtering flask, so the column drains into the test tube. Apply a vacuum to the filtering flask, and add 50 ml 4N HNO₃ to the funnel reservoir. Allow the acid to pass through column and collect in the test tube. The HNO₃ elutes the metal ions from the resin. Wash the resin with a few ml of deionized H₂O and add the wash to the nitric acid solution.

To transfer the cations in the acid solution into a water solution, put the HNO₃ solution in a 100 ml glass beaker and place it on a hot plate to evaporate the acid solution. Take precautions not to "burn" the residue that remains in the beaker. The residue consists of nitrate salts of the trace metals and overheating may oxidize the salts to form insoluble metal oxides. Add 50 ml deionized water to the nitrate salt residue and heat the solution to dissolve the salts. The solution is ready for preconcentration by the batch extraction procedure.

The ion-exchange resin is slowly attacked by the acids. We feel the resin should be replaced after every analysis. However, Danielsson (1965) reports the resin is still usable after three months of daily use, using a similar iron separation procedure.

APPENDIX III

Batch and Column Extraction Procedures

Appendix III describes the extraction (preconcentration) of the metals from solution onto the glass beads. This step is necessary for all rock and water samples. Use the batch extraction procedure when the solution containing the cations is less than 100 ml. For solutions larger than 100 ml, use the column extraction procedure.

Batch Extraction

Place the water solution containing cations in a 250 ml plastic beaker. If the solution volume is less than 50 ml, dilute the solution to 50 ml with deionized water. Adjust the solution to 8.0 ± 0.1 pH with dilute NaOH or dilute HNO₃. Use of pH buffer can replace the acid-base pH adjustments, however, the buffer may react to form a precipitate, and also contaminate the solution. Add 75 mg silylated glass beads (see Appendix I) to the solution. Add a magnetic stir bar and stir the mixture for ten minutes. Monitor the solution pH throughout the stir period and maintain the pH at 8.0. Prepare the beads into a sample pellet immediately after the stir period, according to the instructions in Appendix IV.

Column Extraction

Prepare a column with the same material and dimensions as

the ion-exchange column (Figure 12). Replace the ion exchange resin with 75 mg of silylated glass beads. Attach the column onto the stem of a 200 mm plastic filtering funnel (Gelman, #4203) (figure 14), containing a 25 mm, 0.65 μ m pore size filter. (Millipore, #DAWP 02500). The funnel stem has a single-hole rubber stopper that inserts into a 500 ml filtering flask. Connect the flask to a vacuum hose with a rubber hose. The column apparatus is ready for metal ion extraction.

Place the water solution containing metal ions into a large beaker. Adjust the solution to 8.0 ± 0.1 pH with dilute NaOH or HNO₃. Allow several minutes for pH to stabilize. We do not recommend the use of pH buffer for the column extraction procedure. Place the solution in the reservoir of the filtering funnel, and apply sufficient vacuum to the filtering flask to obtain a flow rate of 10 to 50 ml per minute. After entire solution passes through the column, prepare sample pellet according to instructions in Appendix IV.

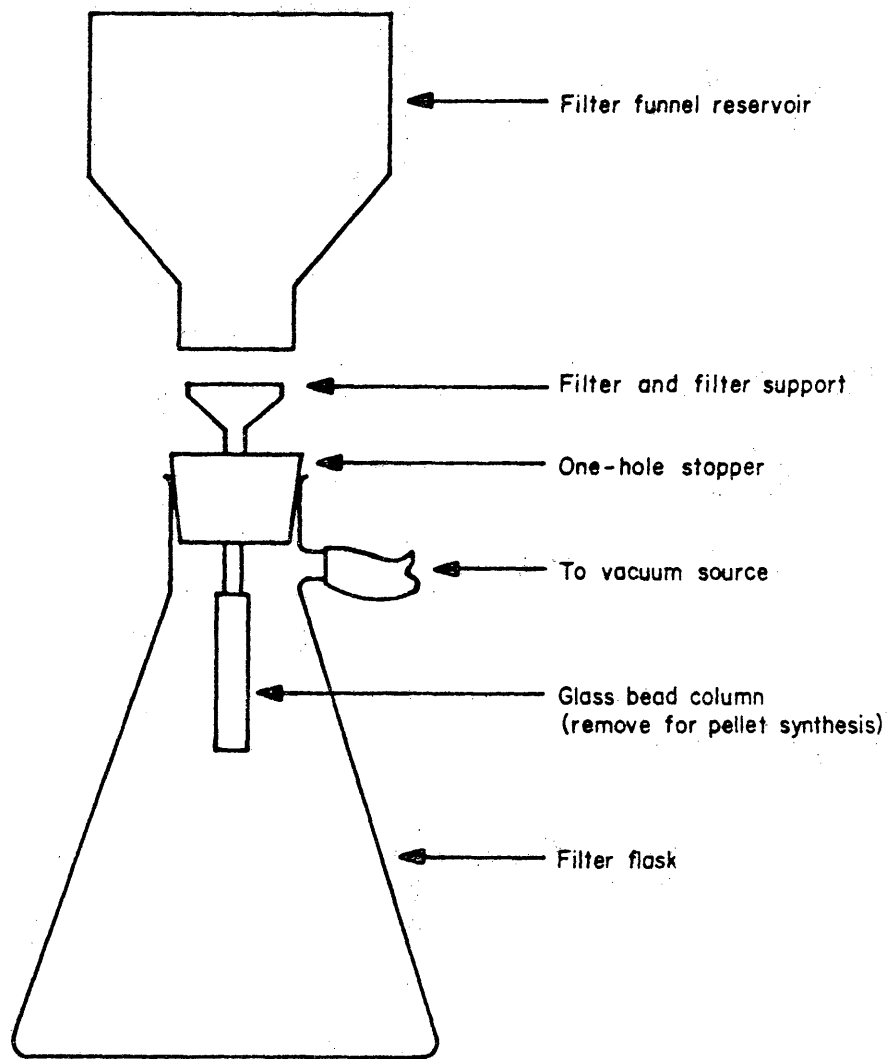


Figure 14 - Apparatus for column extractions and pellet synthesis.

APPENDIX IV

Sample Pellet Synthesis - Procedure and Equipment

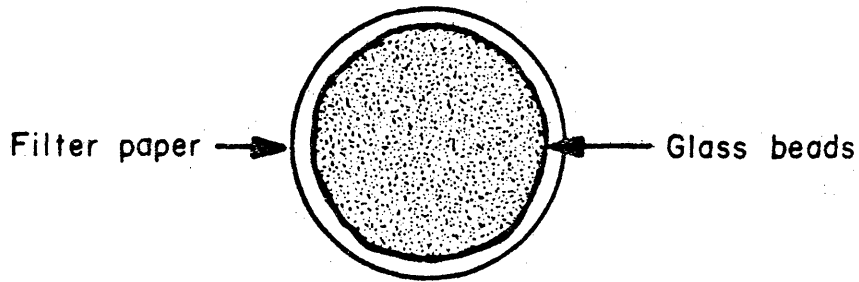
Appendix IV describes our method of making sample pellets from the glass beads. It is possible to eliminate this procedure by use of another sample pellet preparation. Use the same equipment for the pellet preparation as for the column extraction, except remove the extraction column from the filter funnel stem (Figure 14) and place a new 25 mm filter paper in the filter funnel.

Place the glass beads from the column extraction into a beaker with 50 ml of deionized water. The glass beads from a batch extraction are already in this form and this step is not necessary. Pour the glass bead-water mixture into the filter funnel. Wash residual beads from the beaker into the funnel with small quantities of deionized water. Apply a vacuum to the filtering flask to hasten bead recovery from the water solution. Wash beads from funnel sides onto the filter with deionized water and discontinue vacuum. Observe the beads to see if they distribute evenly over the filter surface. Correct any uneven distribution by applying a stream of deionized water to the beads. About 5 ml of water redistributes the beads evenly when they settle. Momentarily reapply the vacuum to drain the water into the flask. The filtering funnel separates at the filter support; remove the top (funnel) portion of the filtering funnel to expose the filter and beads.

Wedge a flat razor blade under the filter and remove the filter, taking care not to disturb the bead distribution on the filter. Place filter on the sample support disk apparatus (Figure 15).

The sample support disk apparatus includes one thin and one thick metal disk. The disk is the primary support disk, and has a rubber seal around the diameter. We call the thin disk the secondary support disk or the radiation enhancer. Place the support disk apparatus, with the filter and beads resting on top, into a 105° C oven to dry for 15 to 20 minutes. Longer drying periods may curl the filter paper, resulting in bead disturbance. Cover the glass bead-support disk apparatus with 3 inch x 3 inch x 0.5 mil. polypropylene film (Somar, #3750-33). Press the sample holder slide over the top of the support disk apparatus to insert the sample into the holder (Figure 16 and 17). Trim excess polypropylene film to complete the sample pellet preparation.

A)



B)

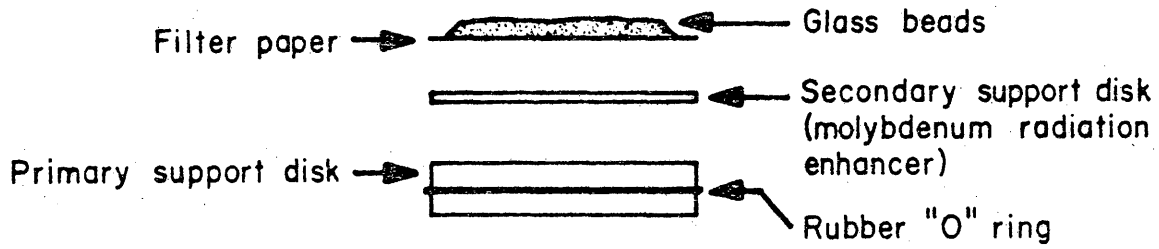
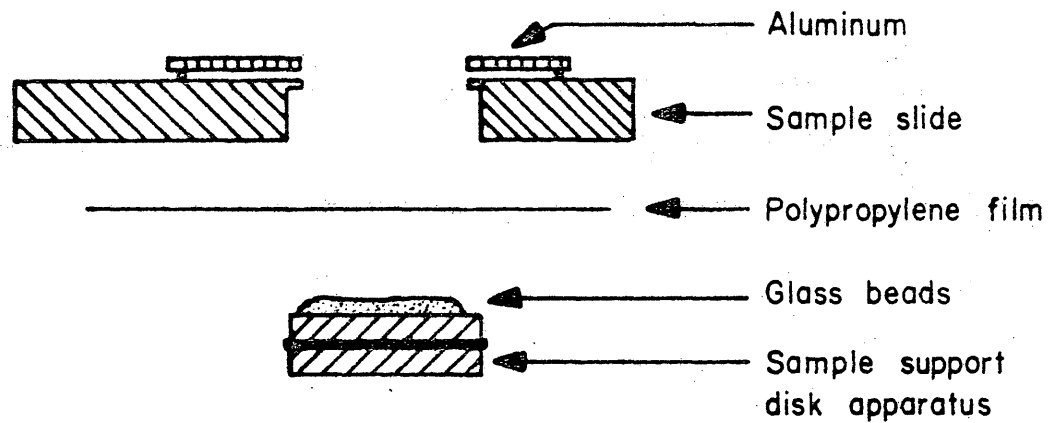


Figure 15 - Sample support disk apparatus. A) Top view, B) expanded side view.

A)



B)

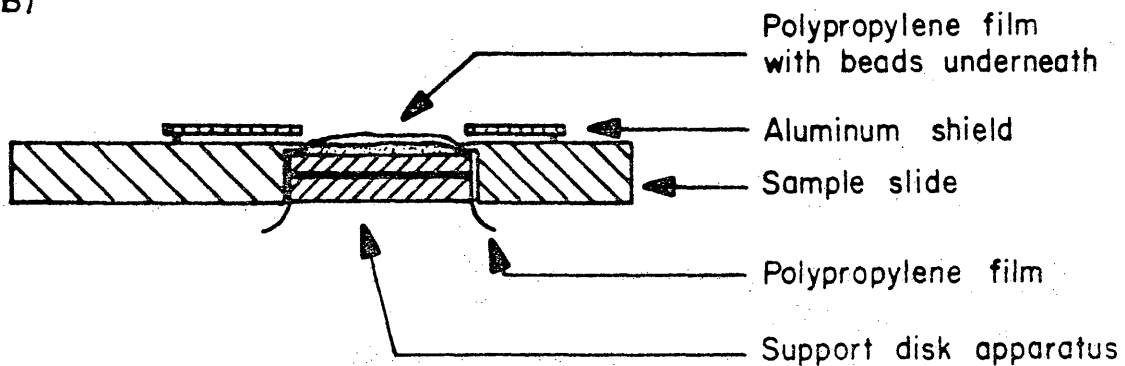


Figure 16 - Sample slide and support disk apparatus (cross-section). A) Sample support disk not inserted, B) inserted.

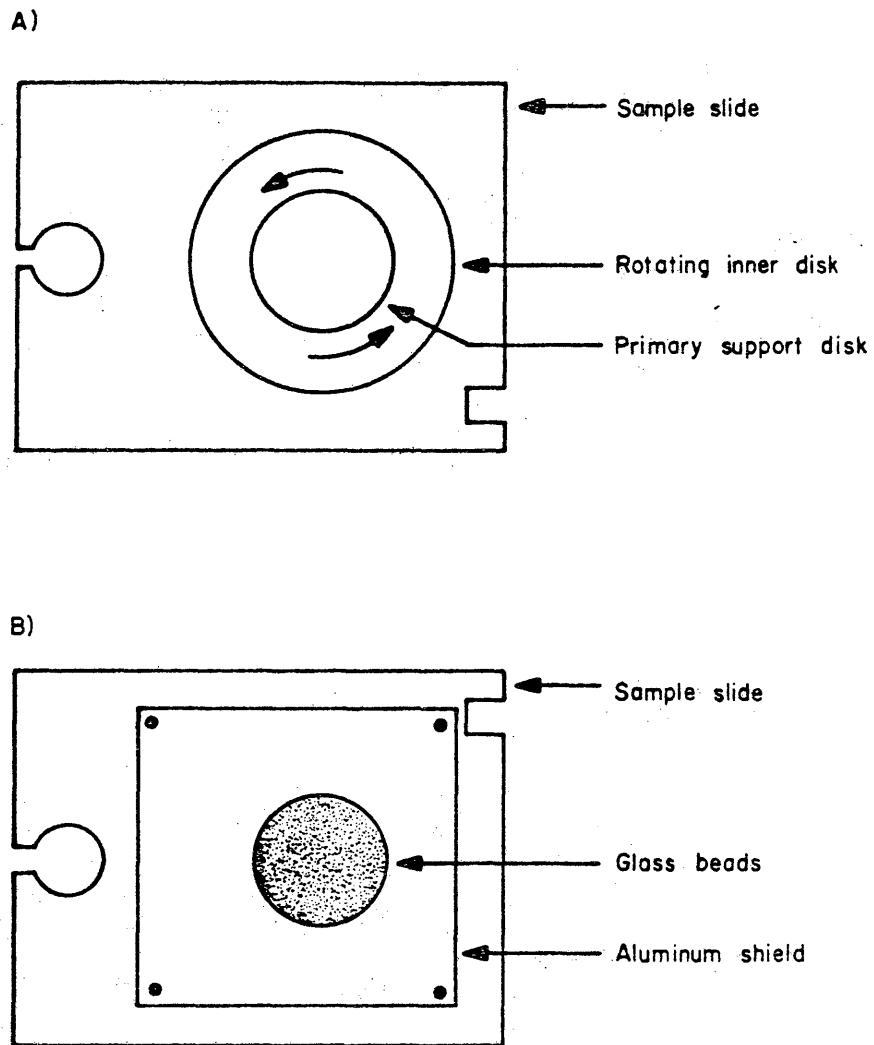


Figure 17 - Sample holder slide with sample support disk inserted. A) Top view, B) bottom view (analyzing surface).

APPENDIX V

Appendix V gives ordering information for special equipment used in this investigation.

- 1) Electro-Nucleonics, Inc.
368 Passaic Avenue
Fairfield, New Jersey 07006
(201) 227-6700

Controlled-pore glass beads, #CPG-240.

- 2) Gelman Instrument Co.
600 S. Wagner Road
Ann Arbor, Michigan 48106
(313) 665-0651

25 mm filter funnel, #4203

- 3) Millipore Corp.
Ashby Road
Bedford, Massachusetts 01730
(617) 275-8800

25 mm filter paper, #DAWP 025 00.

- 4) PCR Research Chemicals, Inc.
P.O. Box 1778
Gainesville, Florida 32602
(904) 376-8946

Dow-Corning Z-6020 (alkoxysilane), #34070-3.

- 5) Sargent-Welch Scientific Co.
P. O. Box 7196
4040 Dahlia Street
Denver, Colorado 80207
(303) 399-8220

5.6 cm, plastic Buchner filter funnel, #5-35620-C.

500 ml plastic filtering flask, #S-34380-E.

- 6) Sigma Chemical Co.
P. O. Box 14508
St. Louis, Missouri 63178
(314) 771-5750

Dowex-50W cation exchange resin, #50X8-200.

- 7) Somar Laboratories, Inc.
P. O. Box 5234
Grand Central Station
N. Y. New York 10017
(212) 697-4351

Spectro-film (polypropylene), #3750-33

- 8) Supelco, Inc.
Supelco Park
Bellefonte, Pennsylvania 16823
(814) 359-2784

Teflon wool, #2-0597

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