1972

# Rapid separation and determination of heavy metals in hydrochloric acid by forced-flow anion exchange chromatography

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RAPID SEPARATION AND DETERMINATION OF HEAVY
METALS IN HYDROCHLORIC ACID BY FORCED-FLOW
ANION EXCHANGE CHROMATOGRAPHY.

Iowa State University, Ph.D., 1972
Chemistry, analytical

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# Rapid separation and determination of heavy metals in hydrochloric acid by forced-flow anion exchange chromatography

by

Mark Donovan Seymour

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Analytical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1972

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# INTRODUCTION

The analysis of metals in complex matrices often requires separation of interfering elements. Numerous chemical and physical separation methods are at the disposal of the analyst but none is more versatile than liquid chromatography (1-3). Recently a scheme was devised for the systematic quantitative separation of 27 different metal ions in a single sample (4).

Ion exchange chromatography is especially suited for separation of metal ions. Chemically stable exchange resins of reasonable purity are commercially available in a variety of mesh sizes. Column preparation is simple and a large body of data has been accumulated on the adsorbabilities of metals in various solvents (5-24).

For ion exchange separation of heavy metals the most popular technique involves use of strongly basic exchange resins in chloride media. In a recent comprehensive review of new analytical methods that involve ion exchange nearly one fourth of all methods reported make use of a resinous quaternary amine exchanger and chloride containing eluents (25). This was twice the number reported for any other system. This wide use reflects the versatility of hydrochloric acid as a solvent for metal ions. Largely because of the complexing power of chloride, a great number of metals form stable solutions in this medium and display a range of adsorbabilities on anion exchange resins.

Unfortunately, inorganic liquid chromatography has been used by some only as a last resort in sample preparation because of long separation times, often 30 minutes per element. In separations where a large difference in adsorbabilities between sample and interferences is not possible, the time of analysis is further increased because of the necessity of using synthetic samples to optimize resolution for the particular sample size, resin, and column dimensions employed.

Recent developments in organic liquid chromatography have enabled a substantial decrease in the time required for optimized separations of mixtures of organic compounds (26). Using pressure to force eluents through small diameter columns of fine mesh resin, thus minimizing flow inequalities while increasing the rate of diffusion limited column processes in order to maintain resolution, separations often have been speeded to one compound per minute. Continuous monitoring of refractive index, conductivity, or ultraviolet absorption of column effluents not only allows optimization of elution conditions but also quantitative estimation of the constituents separated eliminating the need for a subsequent analysis step.

In an effort to apply these techniques in inorganic analysis, a recent paper describes a rapid and selective method for iron(III) using a liquid chromatograph and UV detection (27). Iron(III) is sorbed to a small column of anion exchange resin from 6<u>M</u> hydrochloric acid. This allows concentration of the iron and separation from many interfering elements. Iron(III) is then stripped in more dilute acid and the peak height (in absorbance) of the eluted iron chloro-complex recorded. The amount of iron in the sample is obtained from a linear calibration plot which is constant with time. The dual selectivity afforded by anion exchange and selection of detection wavelength renders a method nearly specific for iron(III).

This technique, arising from the simple combination of anion exchange chromatography and spectrophotometry, would seem applicable to a large number of metal determinations. By simply changing hydrochloric acid concentration, many metal ions first can be strongly sorbed to a bed of anion exchange resin and then selectively eluted (1,3,5). On the other hand, hydrochloric acid has proven a useful reagent for the spectrophotometric determination of a number of elements (28,29).

Herein is described a more comprehensive investigation of the use of forced-flow anion exchange chromatography in the determination of metals in hydrochloric acid. The chromatograph previously described is improved to enable better sensitivity, greater resistance to corrosion and larger pressure capabilities (27). The scope of ultraviolet detection of metal chloro-complexes is investigated. Optimization of selectivity and sensitivity by proper choice of eluent composition and wavelength of detection is illustrated in a method for the rapid determination of lead(II). The problem of rapidly eluting and separating metal ions not desorbable in hydrochloric acid alone is overcome by using a gradient mixture of hydrochloric and perchloric acids. Finally, the separation and quantitative determination of a mixture of several metals is demonstrated.

# THE CHROMATOGRAPH

Although much commercially available equipment has been developed to meet the growing demand for high-speed separation of organic materials, little is suitable for use with the corrosive eluents employed in inorganic analyses. It was therefore necessary to design and construct a chromatograph with the corrosion resistance, rapid eluent change capability and variable detection needed for determination of metals. Operationally similar to the instrument used for determination of iron(III), the chromatograph has been modified as shown in Figure 1 (27).

## Design

Helium is used to force eluents from heavy walled, one-gallon polyethylene bottles and is regulated from 0-55 p.s.i.g. using a Harris Model No. 92-50 regulator. The tested safety factor is 3.6. Gas pressure is applied to the gas pressurization manifold, eluent tanks, pneumatic actuation manifold and sample injection valve through 0.25-in. Dacron pressure tubing. A stainless steel reservoir (capacity 500 ml) is installed between the regulator and pressurization manifold. This allows occasional purging of the manifold with water and acetone to inhibit corrosion and prevent eluent contamination. Pressure is applied to the eluent tanks through specially machined Kel-F fittings attached to the Teflon cap as shown in Figure 2. Liquid escapes through the cap which acts as a

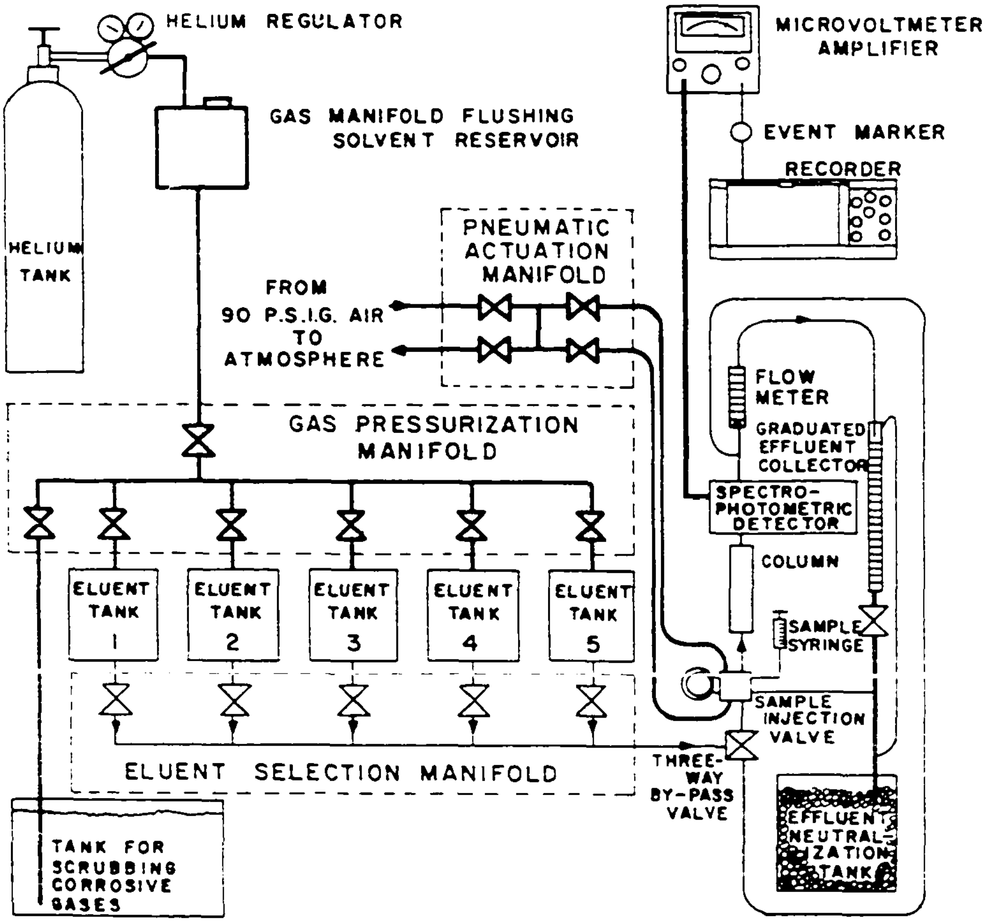

Figure 1. Schematic diagram of liquid chromatograph

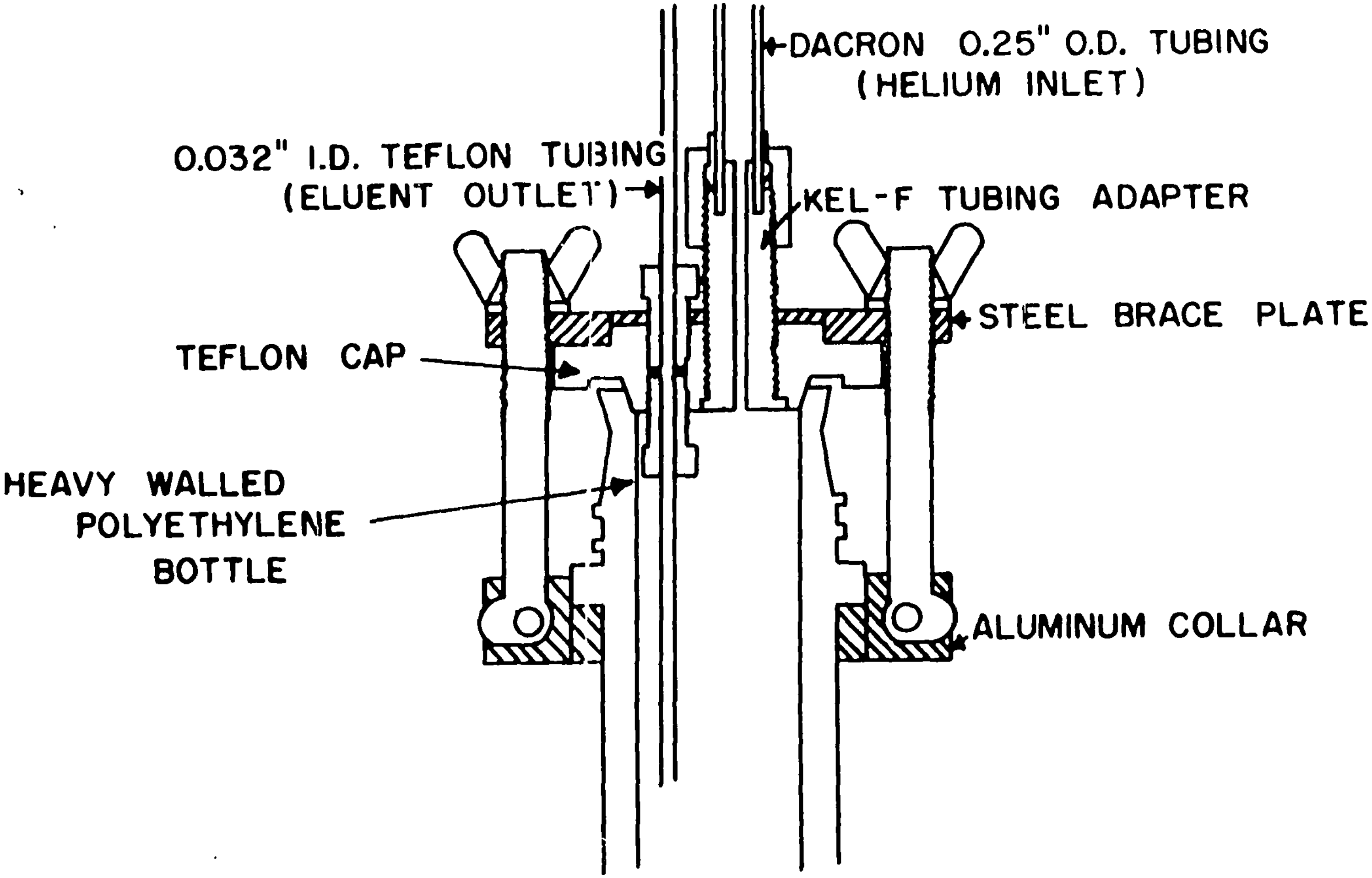

Figure 2. Cross section of eluent bottle cap

coupling for the interior and exterior 0.031-in. i.d. Teflon tubing. The eluent bottles are encased in 6-in. iron pipe welded to a 0.25-in. iron base plate. A circular metal plate with a hole for the neck holds the bottle firmly in place.

Pressurization of the actuation manifold, which consists of four Hoke No. 1511M2B snap valves used to pressurize two PA-875-K actuators, is accomplished using compressed air at 90 p.s.i.g.

The valves, actuators, columns, tube-end fittings and connecting tubing used in eluent manipulation were either obtained from Chromatronix, Inc. or were specially designed to adapt to or replace same. The eluent tanks are connected to five "Cheminert" CAV-2031-K valves for eluent selection. These are in turn connected to a six port union machined from a single Kel-F block. A CAV-3031-K three way valve is used to connect the union with either the sample injection valve or by-pass loop. The by-pass loop, the other end of which is connected to a Kel-F tee between the detector and the flow meter, is used for purging air from the selection manifold and flow meter. The volume between eluent selection valves and column is minimized to allow rapid change of eluents with negligible mixing.

The SV-8081-K sample valve is used to inject reproducibly samples as small as 40 μl. Sample volume depends on the length of the sample loop installed. Samples as large as 10 ml can be easily accommodated. In the "Fill loop" position eluent is allowed to flow directly through the valve and into the analytical column. This, at the same time, allows filling of the sample loop using a syringe. When the valve is thrown to the "Inject" position, the eluent is forced through the sample loop sweeping the sample into the column.

The chromatograph is designed to accept any Chromatronix column; however, 6.35-mm i.d. columns were found most useful for the work described. The column outlet is connected to the inlet of a 1.00-cm path length z-configuration flow-through cell. The cell, as shown in Figure 3, is mounted immediately adjacent to the phototube compartment in a Coleman Hitachi Model 101 UV-visible spectrophotometer. It is constructed of a Kel-F body with opaque Teflon caps holding 1-mm quartz windows. The cell has an aperture diameter of 2 mm, and an internal volume of only 32 µl. This design minimizes loss of resolution due to mixing but necessitates amplification of spectrophotometer output. This is accomplished by installing a Kaylab Model 202B microvoltmeter between spectrophotometer and recorder. The Model SRLG recorder was obtained from E. H. Sargent and Company and is capable of linear (transmittance) or logarithmic (absorbance) display. The recorder is equipped with a Disc Instruments, Inc. Model 204DM integrator. An event marker was constructed by connecting a 1000 ohm resistor in series with a tap key across the recorder input terminals.

The effluent passes from the detector through a Rogers Gilmont Instruments, Inc., catalog No. 3201, size No. 1 flow-

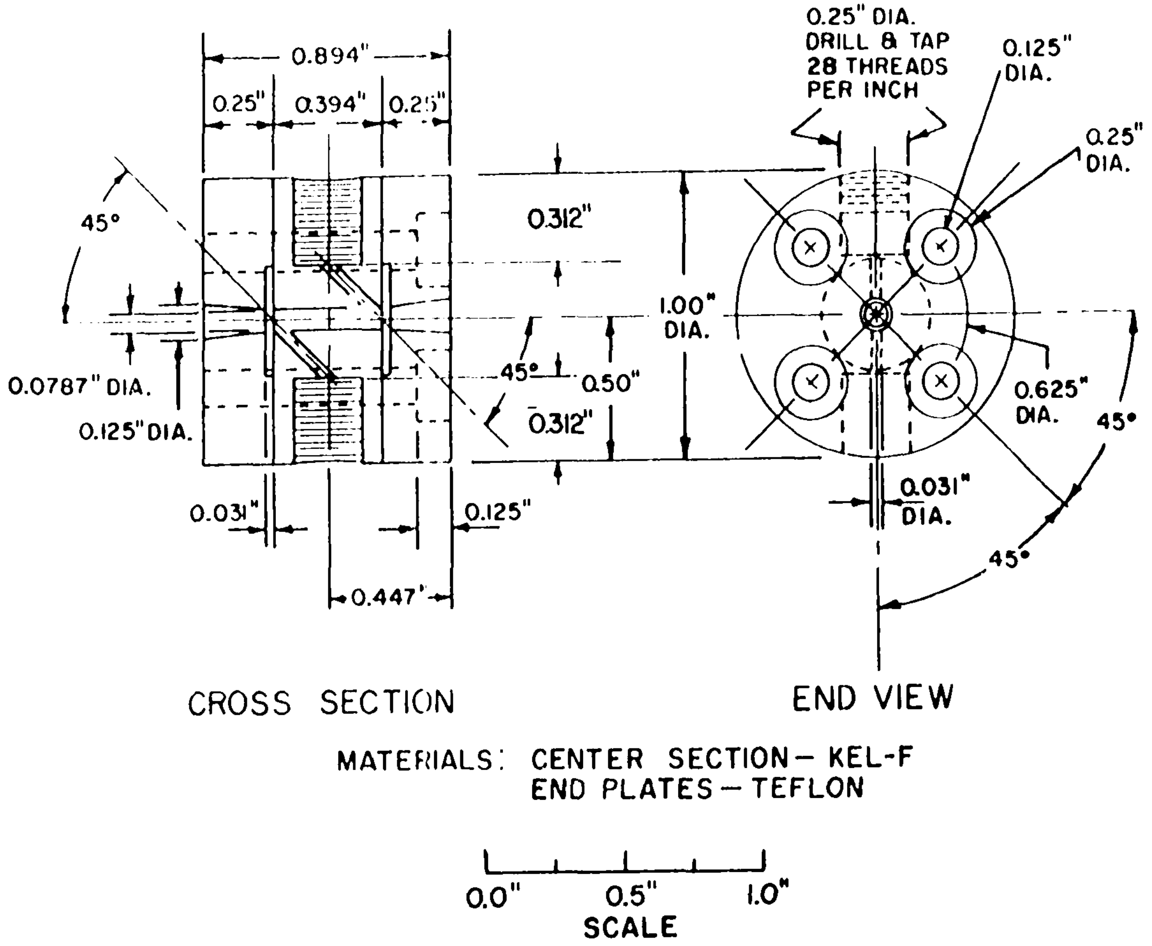

Figure 3. Flow-through cell

meter and then into a 10-ml graduated effluent collector. The latter is used for calibration of the flowmeter and determination of small retention volumes. Below the collector the effluent, along with waste from the sample valve, is drained into an effluent neutralization tank. This tank contains a bed of crushed limestone one foot deep and is capable of increasing effluent pH up to five units.

The chromatograph is thus constructed so that only Kel-F, polyethylene, Teflon and glass contact the liquid enabling use of a wide variety of solvents.

## Operational Notes

Unlike chromatographs which operate at constant flow rate, using pumps to supply the pressure necessary to maintain that flow rate, this chromatograph operates at constant pressure. Experience has proven certain procedures helpful in operation of this type of instrument.

It is often necessary to determine the relationship between flowmeter reading and flow rate for the eluent(s) employed. This is best done by calculation of a pair of constants peculiar to a particular eluent and the particular flowmeter. The relationship between flow rate (F) and flowmeter scale reading (S) can be expressed as follows:

$$F = AS^2 + BS$$

where A and B are constants dependent on the viscosity and density of the liquid and the dimensions of the meter. By careful determination of two flow rates (timing collection of at least 5 ml of eluent) which correspond to flowmeter readings at approximately 80% and 35% full scale, simultaneous equations can be solved for A and B. Once A and B are known the scale reading corresponding to a particular flow rate can be calculated. It is also worthy of note that in plotting molarity of hydrochloric acid versus the flowmeter scale reading corresponding to 1.00 ml/min, a straight line is obtained from water to 10M hydrochloric acid. This allows prediction of the scale readings corresponding to a given flow rate for all concentrations of hydrochloric acid from two sets of flow meter constants or only four experimentally determined flow rates.

In separation of metal ions it is often necessary to employ large changes in eluent composition. When operating at constant pressure, this usually results in a change of flow rate. This change can arise from shrinking or swelling of the resin, which alters column flow resistance, or more likely from a change in eluent viscosity. This, however, has been found to cause no problem with reproducibility of chromatographic data. Even though applied pressure is directly proportional to the flow rate of a given eluent, attempts to manipulate pressure to maintain constant flow rate on changing eluents are infeasible because of difficulty in rapid or precise setting of the regulator. It is best to set the regulator to give a desired flow rate in the first eluent used in the separation and hold pressure constant adjusting when necessary between separations. In doing so it is important to appreciate the flow resistance of the sample loop, setting the regulator with the sample valve in the "Inject" position.

Another problem arising with constant pressure applications is a change in the column flow resistance caused by incomplete removal of fine resin particles before packing the column. This manifests itself in a gradual increase in the pressure necessary to maintain a constant flow rate because of clogging of the filter disc at the column exit. If this is the case, reversal of the column will result in a flow rate increase as some of these fine particles dislodge from the clogged disc. All fines can be removed from these discs by boiling in a mixture of concentrated nitric and perchloric acids. The ground resins thus far tested have all caused eventual clogging despite repeated flotation of fine resin particles. Bead type resins, on the other hand, were used for extended periods of time with no detectable change in column pressure drop. It should be noted that when using identical columns, applied pressures, and resin mesh sizes the flow rate is much greater with spherical resin beads than with ground resin. To minimize particle size and maintain reproducible flow rates, spherical resin beads should be used whenever possible.

Problems with removal of air from the flowmeter and eluent manifold have been solved by installation of the three way by-pass valve. This allows the pressurized eluent to by-pass the column and detector (and resulting pressure drop) causing an increase in flow rate and forcing trapped air from the system. Entrapment of air in changing columns is best avoided by checking for bubbles in the column leads or connecting tubing to the detector and sample injection valve. This is accomplished by using excess solvent in packing the column so that upon insertion of the outlet plunger solvent is forced to escape through both column inlet and outlet. The outlet is then capped and the inlet is connected to the sample injection valve with a stream of water flowing through the chromatograph. This ensures that air will be forced from the couplings as the tube ends are joined. Next, the outlet is uncapped and connected to the detector again with water flowing.

Despite these efforts air sometimes collects in the flow-through cell. Often air will pass through the cell if it is mounted with the outlet at the top. If not, forcing a rapid stream of solvent through the detector cell with a syringe will dislodge any remaining air. Air trapped in the detector will cause erratic response sensitive to flow rate. It may appear as an absorbance increase in the form of sharp erratic peaks or as a constant baseline shift. Before disassembly of the instrument the possibility of air should always be checked.

Finally, it should be mentioned that when operating in the ultraviolet portion of the spectrum where amplification of spectrophotometer output is necessary, the best signal to noise ratio is obtained using low voltage (high gain) ranges on the microvoltmeter and the highest voltage range on the recorder.

## SPECTROPHOTOMETRIC DETECTION

Although methods have been reported for continuous monitoring of column effluents in the chromatographic separation of metal ions, the use of ultraviolet absorption detectors has been largely overlooked. However, this technique has proven most useful in organic liquid chromatography (26). Because of the great number of compounds detectable and the insensitivity of these detectors to changes in flow rate and temperature, this method of detection is by far most popular in high speed organic analysis. Signal attenuation is possible and detectors are available with sensitivities of 0.005 absorbance units full scale with ± 1% noise.

To better determine the number of metal ions that can be detected in a similar fashion, the UV absorption spectra of 70 metals, dissolved in 6$\underline{M}$ hydrochloric acid, were obtained. Over half of these ions display molar absorptivities greater than 100 in the region from 400 nm to the cutoff for hydrochloric acid at 210 nm. In contrast to the broad absorption of organic compounds in this region, the spectral features of these ions are in general sharp, providing for selectivity in choice of detection wavelength. Good sensitivity is promised for some elements with molar absorptivities in excess of 10,000.

## Experimental

Apparatus. A Cary Model 14 Serial 19 recording spectrophotometer with 1.00-cm cells was used to obtain the spectra of the metal ions studied.

Reagents. Metal solutions were prepared by dissolving oxides, chlorides, or high purity metals in hydrochloric acid. The solutions were transferred to a tared container and diluted to weight. Special procedures were used to obtain solutions of a few ions. Arsenic(III) and germanium(IV) were prepared by first dissolving the appropriate oxides in a solution of sodium hydroxide before addition of hydrochloric acid. Antimony(V) oxide was dissolved in concentrated acid before dilution. Calcium carbonate, thorium nitrate, and uranyl acetate were converted to the chloride salts by heating to dryness in concentrated hydrochloric acid. Iron(III) and rhenium(VII) were prepared from the metals by treatment with a mixture of hydrogen peroxide and acid. Titanium(III) was prepared by dissolving the metal in hydrochloric acid. Titanium(IV) was prepared from titanium(III) by oxidation with peroxide and subsequent destruction of the peroxo-complex with strong acid and heat. Spectral studies show at least 99% conversion of oxidation states. Vanadium(IV) was prepared by reduction of vanadium(V) in ethanolic hydrochloric acid.

Solutions of chromium(VI), silver(I), and vanadium(V) were prepared immediately before obtaining their spectra as these ions are reduced in this medium.

All chemicals were reagent grade except for the high purity lanthanide oxides obtained from the Ames Laboratory. The metals dissolved were at least 99.99% pure. For use in this survey weighings based on formula weights were assumed absolute; no independent standardization of solutions was attempted. All spectra were recorded against a 6M hydrochloric acid blank.

## Results and Discussion

The spectra of 36 metal ions in 6M hydrochloric acid are shown in Figures 4-12. Table I gives a summary of the ions examined and their maximum molar absorptivities in the ultraviolet. Examination of these data demonstrates the versatility of this method of detecting heavy metals in chloride bearing eluents. Monitoring at 225 nm allows detection of a large number of metals. Although few metal complexes display maxima at this wavelength, all show at least shoulder absorption. Even detection of arsenic(III), cadmium(II), chromium(III), europium(III), indium(III), manganese(II), nickel(II), rhenium (VII), titanium(III), titanium(IV), vanadium(V), and zirconium(IV) which have maxima below the hydrochloric acid cutoff, is possible at 225 nm. Other ions including antimony(V), antimony(III), bismuth(III), cerium(III), chromium(VI), gold (III), lead(II), mercury(II), palladium(II), platinum(IV), rhodium(III), silver(I), thallium(III), tin(II), tin(IV) and terbium(III) display one or more sharp maxima in the UV enabling some degree of selectivity by careful selection of wavelength. Finally, a group of metal ions including copper (II), iron(III), molybdenum(VI), ruthenium(III), and uranium (VI) absorb throughout this region. These ions have moderate to strong absorption and are likely to interfere with detection. Separation from this group is, therefore, a necessary prerequisite for spectrophotometric determination of a given metal.

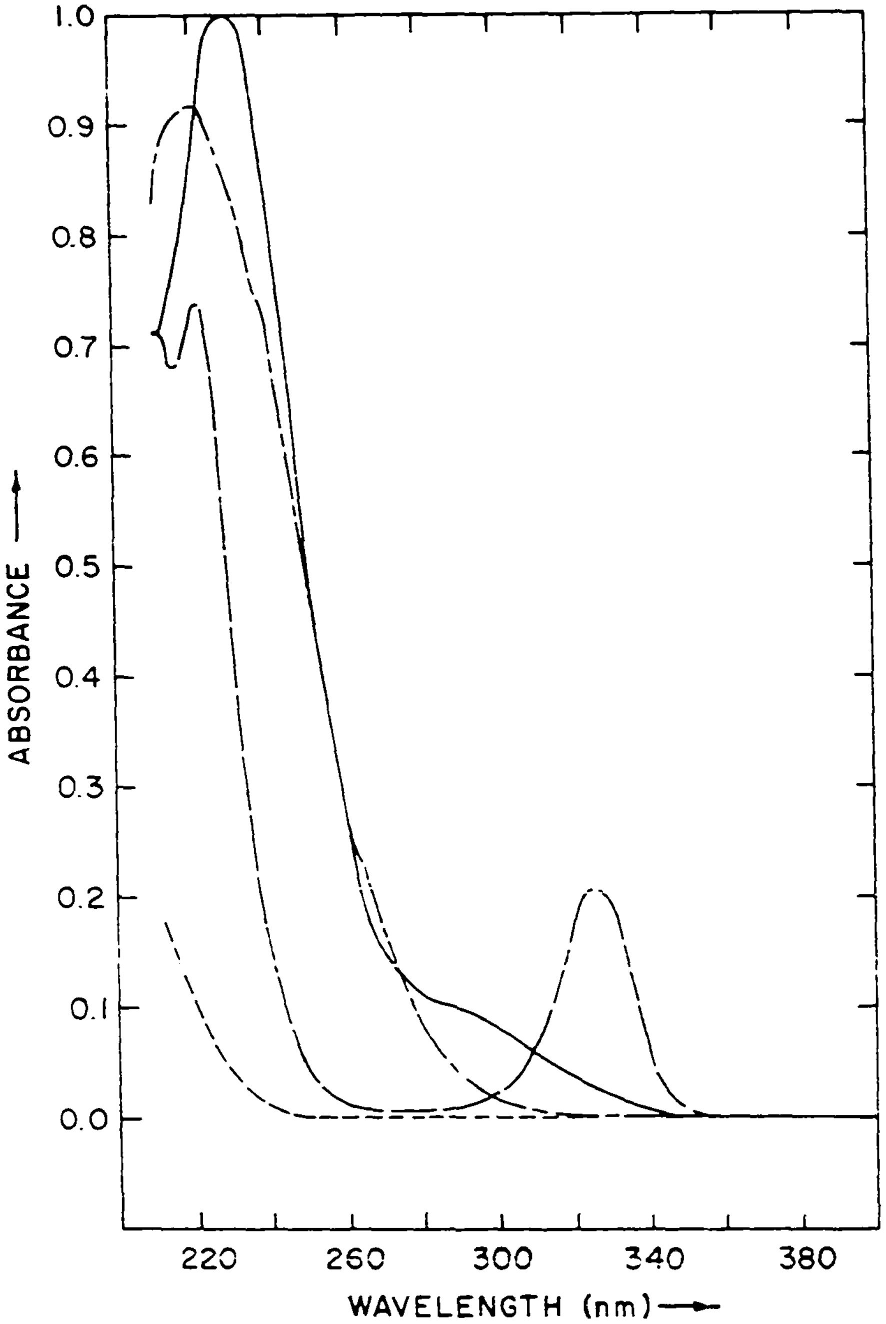

Figure 4. Spectra of antimony(V), antimony(III), arsenic(III), and bismuth(III) in 6M hydrochloric acid

__ _ __ 40 ppm Sb(V), _______ 5 ppm Sb(III),

_ _ _ _ 1 ppm As(III), ___ ___ 3 ppm Bi(III)

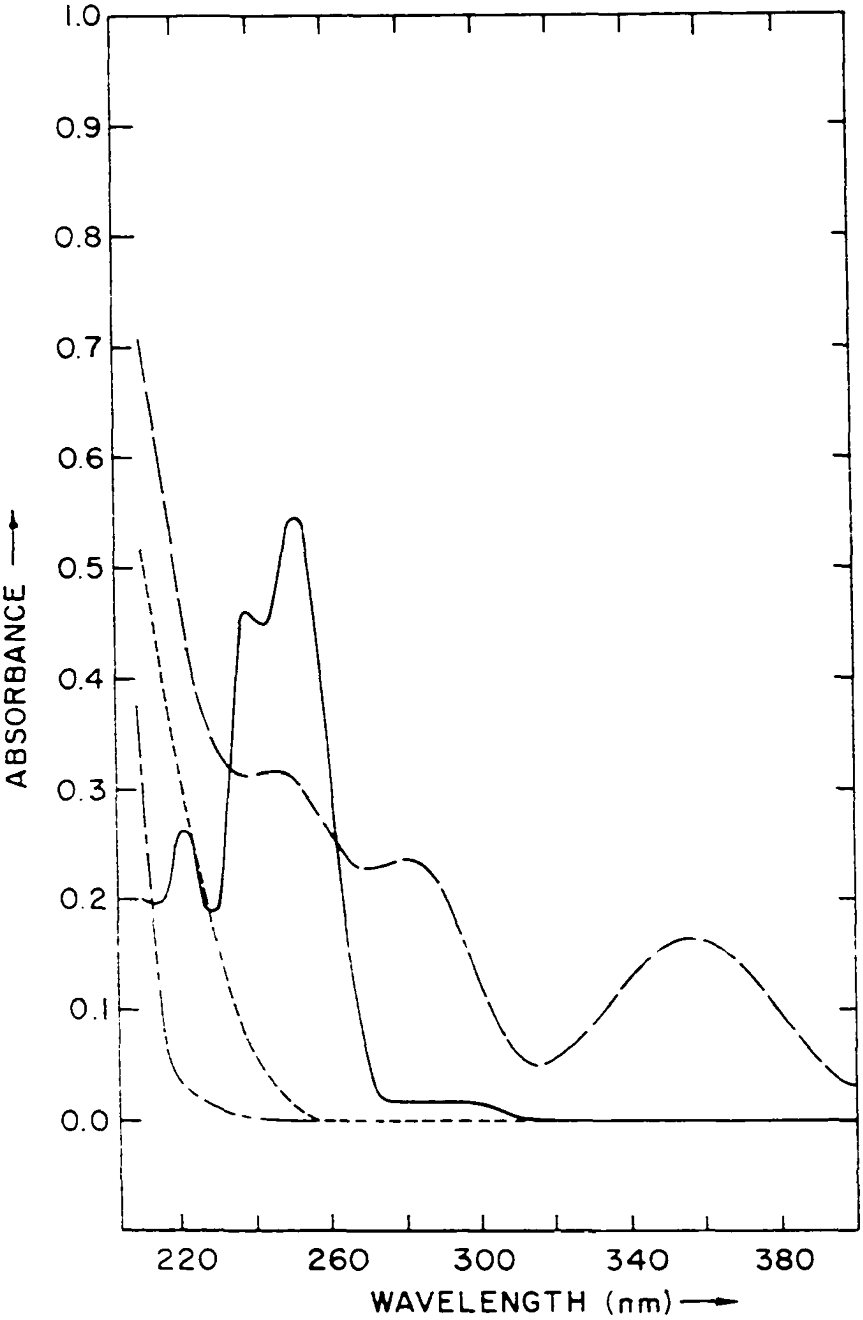

Figure 5. Spectra of cadmium(II), cerium(III), chromium(III), and chromium(VI) in 6M hydrochloric acid

__ _ __ 100 ppm Cd(II), _______ 100 ppm Ce(III),

_ _ _ _ 5 ppm Cr(III), ___ ___ 8 ppm Cr(VI)

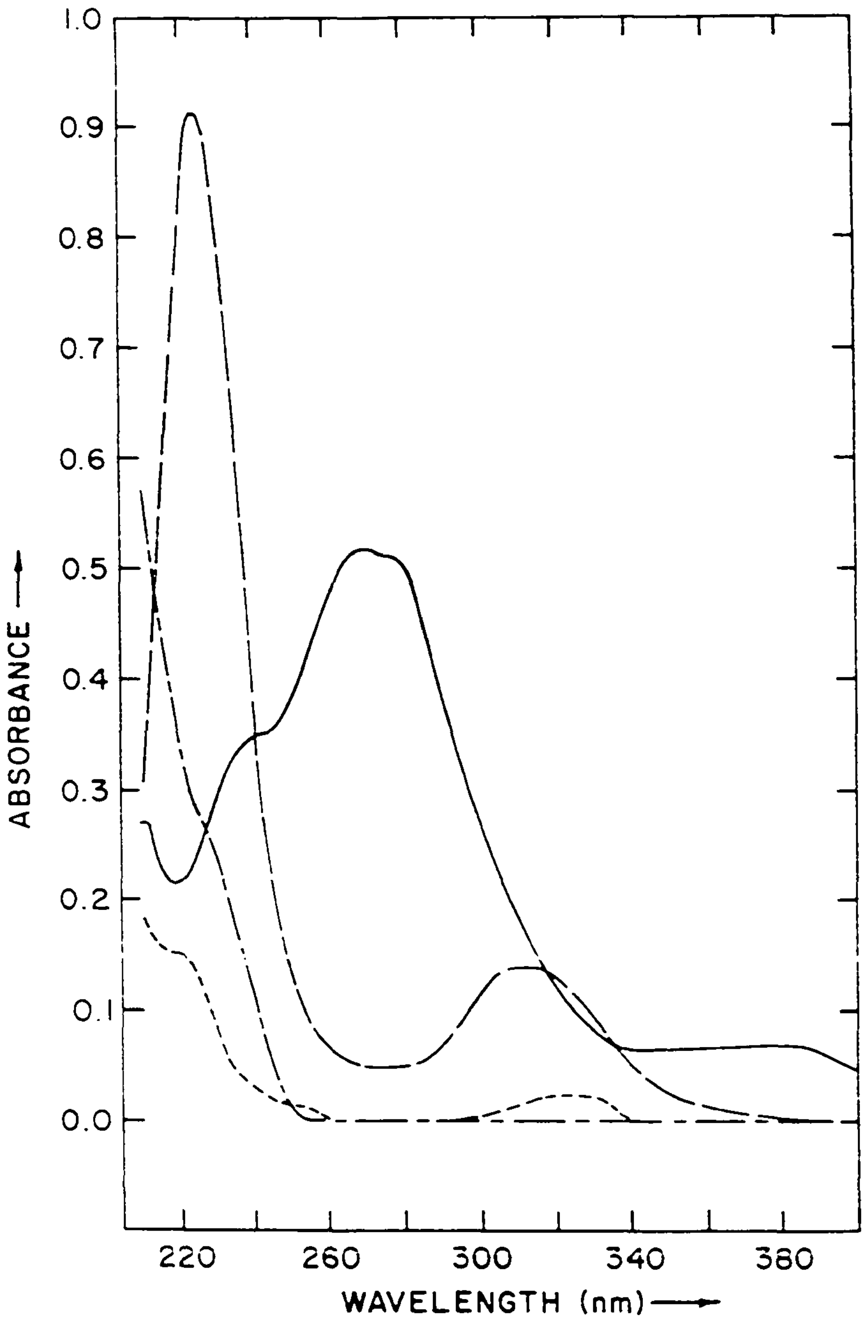

Figure 6. Spectra of cobalt(II), copper(II), europium(III), and gold(III) in 6M hydrochloric acid

__ _ __ 100 ppm Co(II), _______ 10 ppm Cu(II),

_ _ _ _ 100 ppm Eu(III), ___ ___ 5 ppm Au(III)

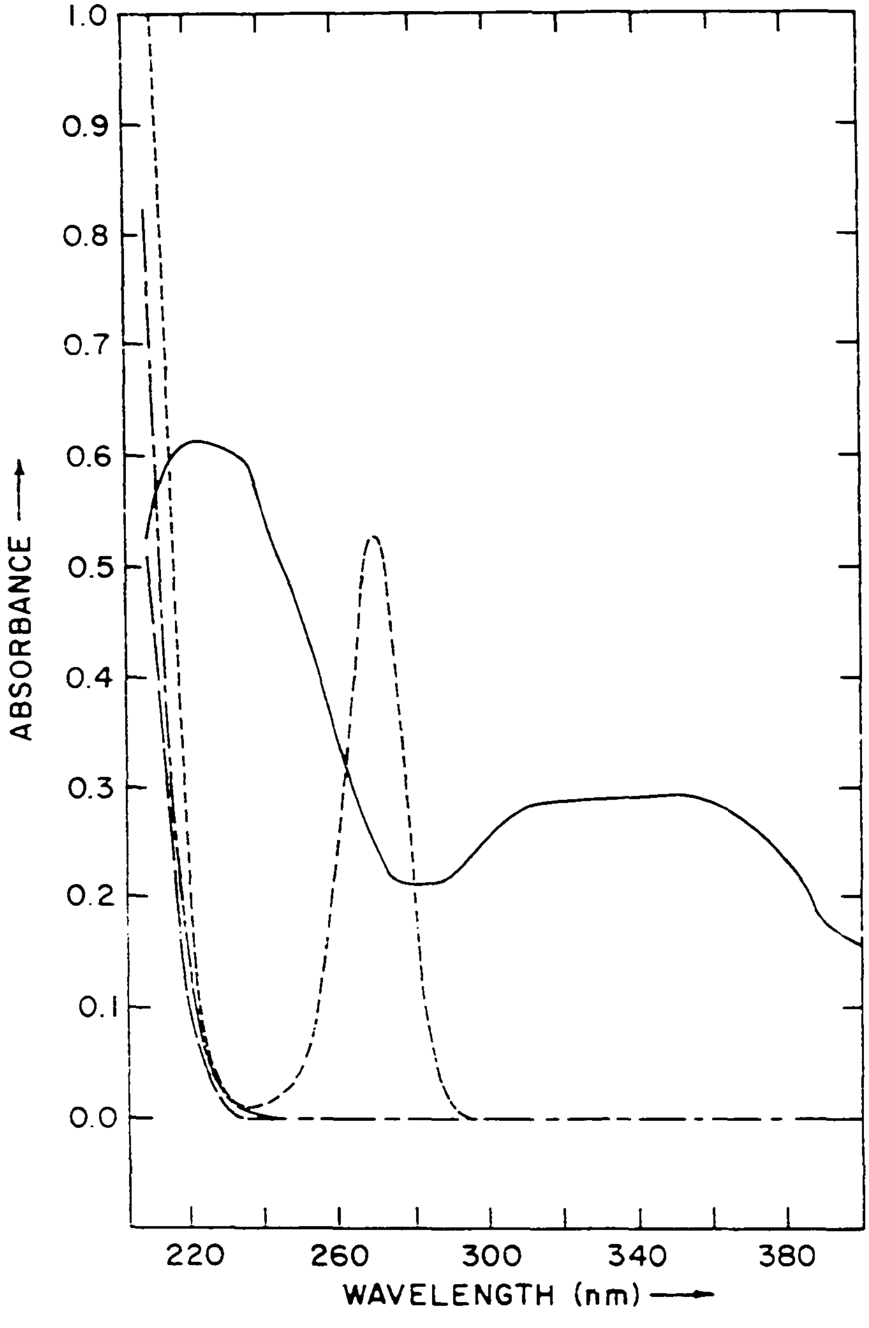

Figure 7. Spectra of indium(III), iron(III), lead(II), and manganese(II) in 6M hydrochloric acid

__ _ __ 50 ppm In(III), _______ 5 ppm Fe(III),

_ _ _ _ 10 ppm Pb(II), ___ ___ 100 ppm Mn(II)

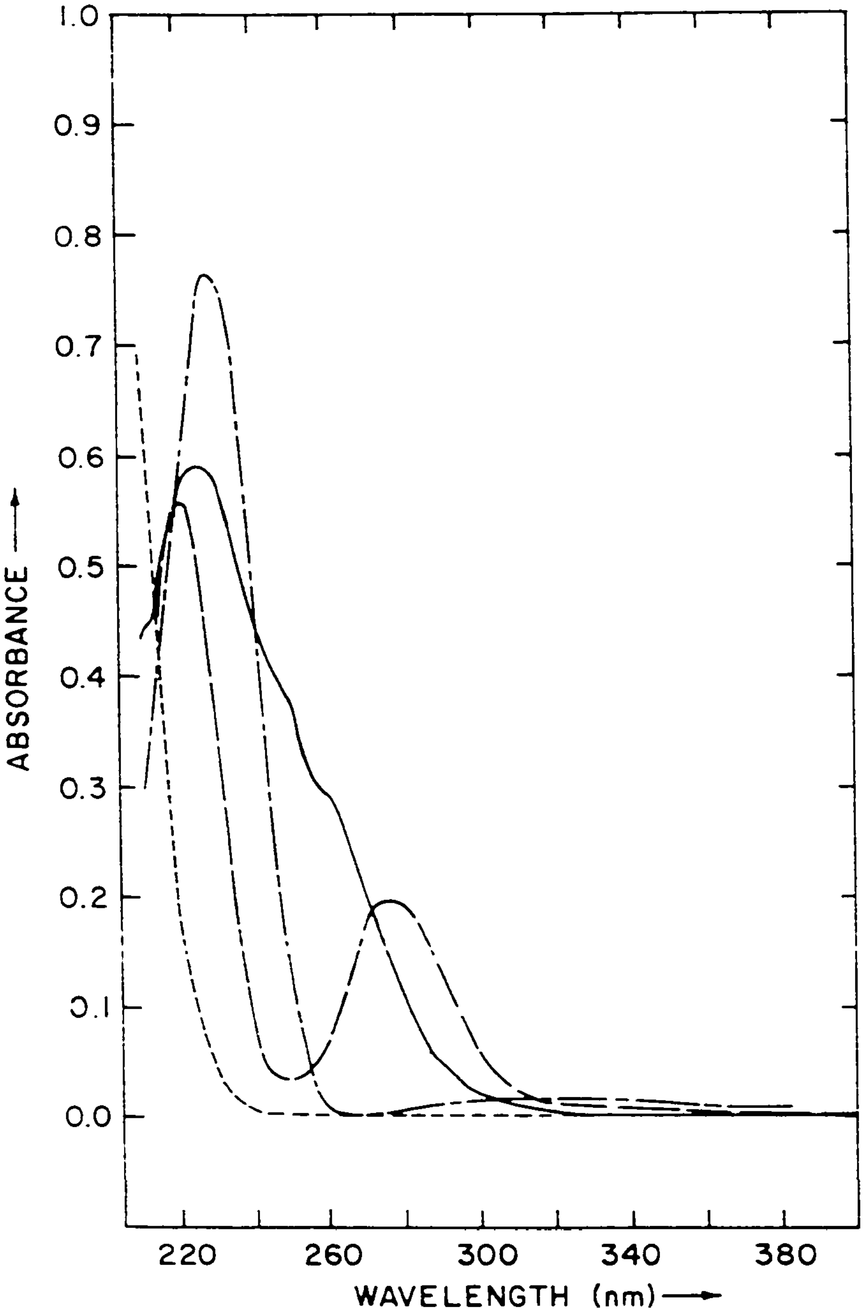

Figure 8. Spectra of mercury(II), molybdenum(VI), nickel(II), and palladium(II) in 6$\underline{M}$ hydrochloric acid

— - — 5 ppm Hg(II), ——— 10 ppm Mo(VI),

- - - - 150 ppm Ni(II), — — 1 ppm Pd(II)

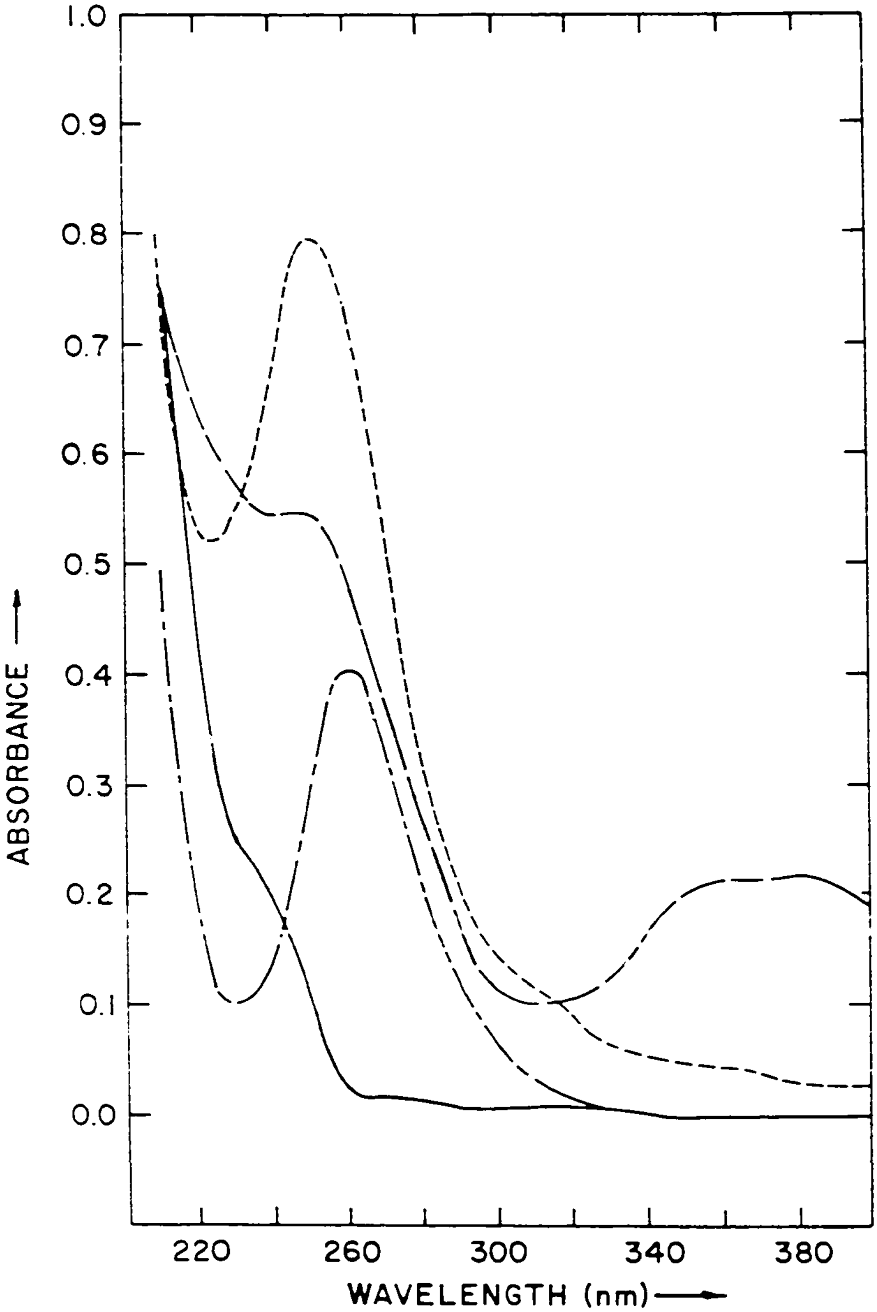

Figure 9. Spectra of platinum(IV), rhenium(VII), rhodium (III), and ruthenium(IV) in 6M hydrochloric acid

__ _ __ 3 ppm Pt(IV), _______ 5 ppm Re(VII),

_ _ _ _ 5 ppm Rh(III), ___ ___ 4 ppm Ru(IV)

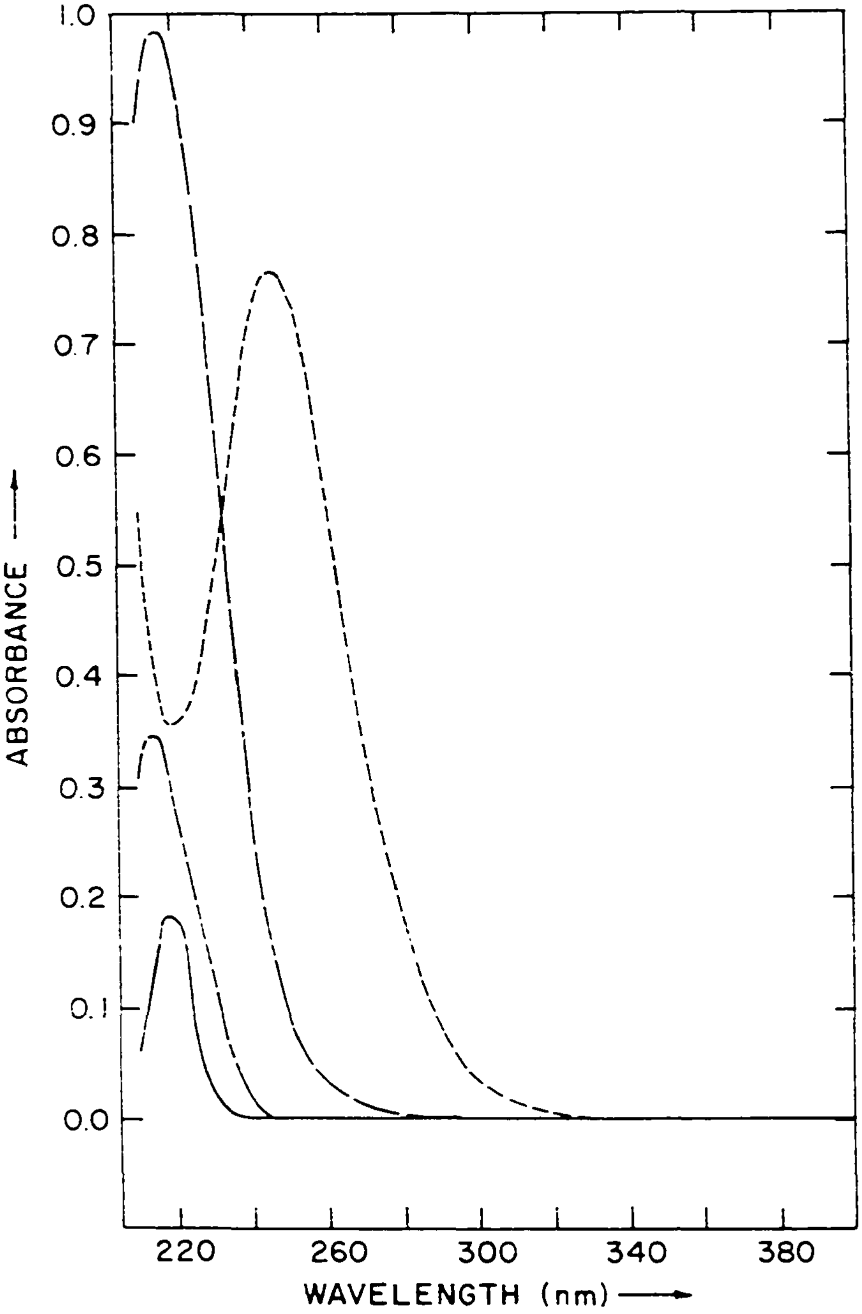

Figure 10. Spectra of silver(I), terbium(III), thallium(III), and tin(IV) in 6$\underline{M}$ hydrochloric acid

__ _ __ 2 ppm Ag(I), _______ 100 ppm Tb(III),

_ _ _ _ 10 ppm Tl(III), ___ ___ 10 ppm Sn(IV)

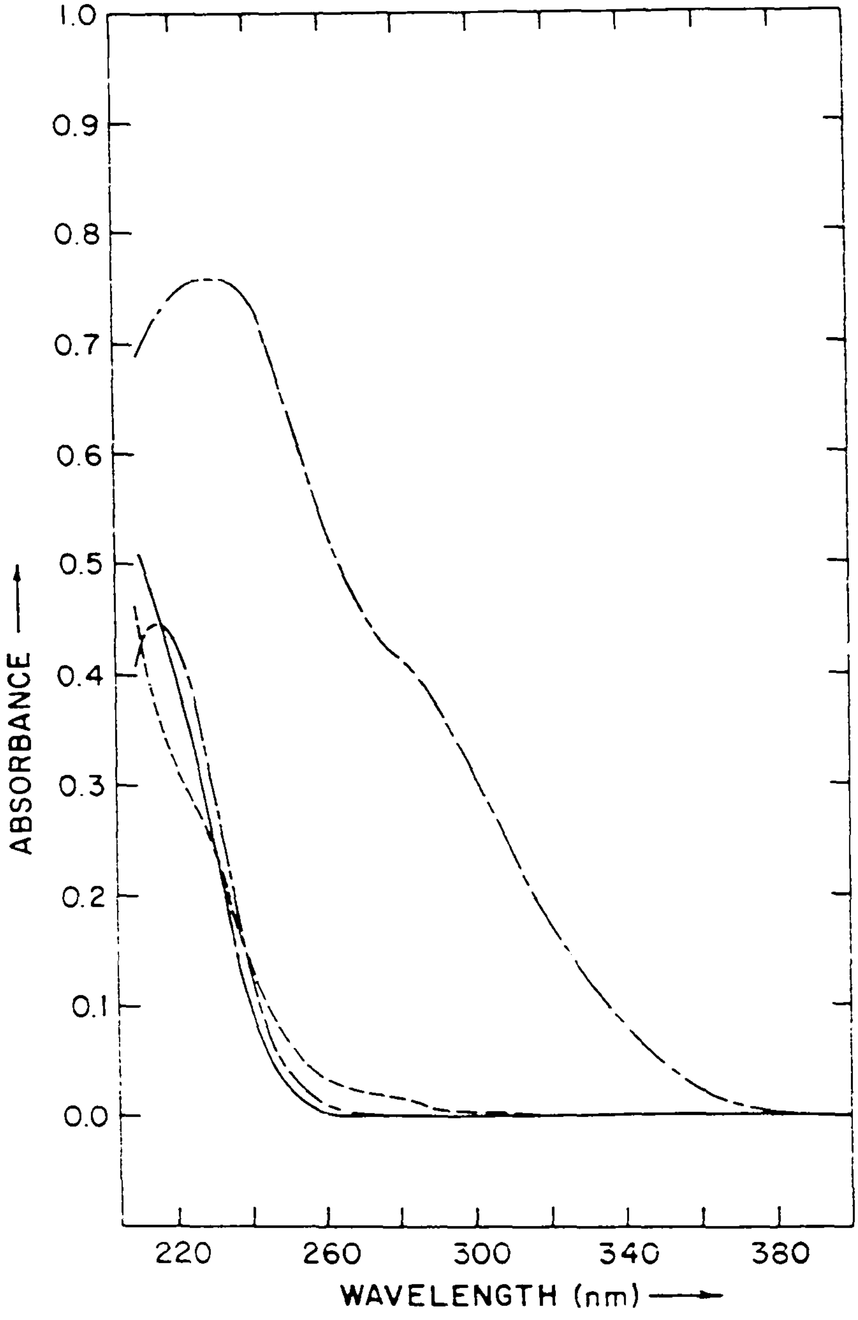

Figure 11. Spectra of tin(II), titanium(III), titanium(IV), and uranium(VI) in 6$\underline{M}$ hydrochloric acid

__ _ __ 5 ppm Sn(II), ________ 20 ppm Ti(III), _ _ _ _ 20 ppm Ti(IV), ___ ___ 50 ppm U(VI)

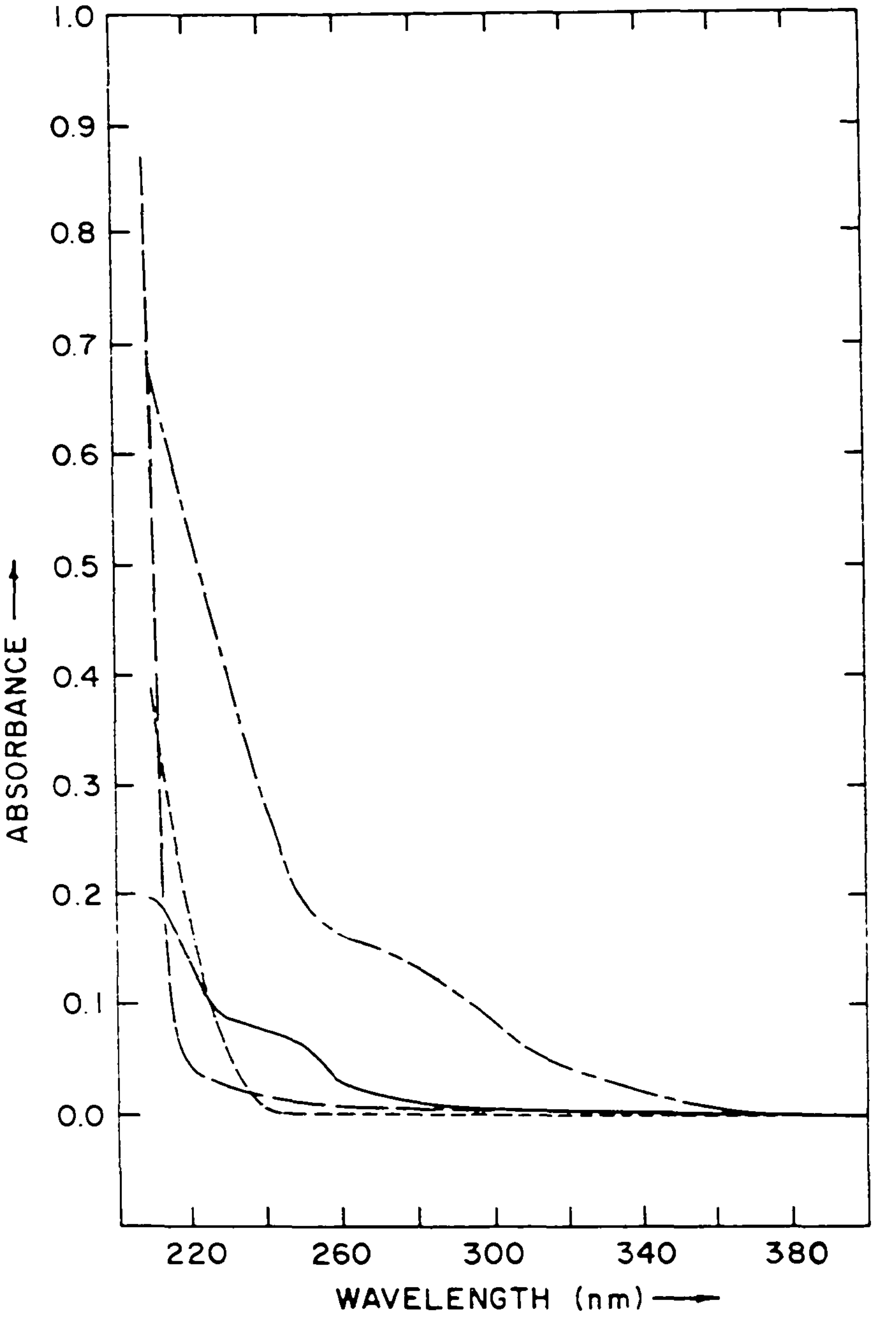

Figure 12. Spectra of vanadium(V), vanadium(IV), and zirconium(IV) in 6M hydrochloric acid; and the cutoff for 6M hydrochloric acid versus water

__ _ __ 10 ppm V(V), _______ 10 ppm V(IV),

_ _ _ _ 100 ppm Zr(IV), ___ ___ 6M HCl

Table I. Maximum Ultraviolet Molar Absorptivities for Metal Ions in 6M HCl

| | |
|---|---|
| Al(III) | N[a] |
| Sb(III) | 25,000 |
| Sb(V) | 6,300 |
| As(III) | 12,000 |
| As(V) | $\sim$24 |
| Ba(II) | N |
| Be(II) | N |
| Bi(III) | 47,000 |
| B(III) | N |
| Cd(II) | 400 |
| Ca(II) | N |
| Ce(III) | 700 |
| Cs(I) | N |
| Cr(III) | 5,000 |
| Cr(VI) | 4,250 |
| Co(II) | 310 |
| Cu(II) | 3,100 |
| Dy(III) | N |
| Er(III) | $\sim$80 |
| Eu(III) | 250 |
| Gd(III) | N |
| Ga(III) | N |
| Ge(IV) | N |
| Au(III) | 33,000 |
| Hf(III) | $\sim$50 |
| Ho(III) | N |
| In(III) | 1,800 |
| Fe(III) | 6,300 |
| La(III) | N |
| Pb(II) | 10,000 |
| Li(I) | N |
| Lu(III) | N |
| Mg(II) | N |
| Mn(II) | 260 |
| Hg(II) | 28,000 |
| Mo(VI) | 5,200 |
| Nd(III) | N |
| Ni(II) | 260 |
| Nb | I[b] |
| Pd(II) | 54,000 |
| P(V) | N |
| Pt(IV) | 30,000 |
| K(I) | N |
| Pr(III) | $\sim$52 |
| Re(VII) | 13,000 |
| Rh(III) | 15,000 |
| Rb(I) | N |
| Ru(IV) | 15,000 |
| Sm(III) | N |
| Sc(III) | N |
| Ag(I) | 17,000 |
| Na(I) | N |
| Sr(II) | N |
| Ta | I |
| Tb(III) | 270 |
| Tl(III) | 14,000 |
| Th(IV) | N |
| Tm(III) | N |
| Sn(II) | 9,800 |
| Sn(IV) | 11,000 |
| Ti(III) | 1,100 |
| Ti(IV) | 1,000 |
| W | I |
| U(VI) | 3,300 |
| V(IV) | 900 |
| V(V) | 3,200 |
| Yb(III) | N |
| Y(III) | N |
| Zn(II) | N |
| Zr(IV) | 320 |

[a] No absorption at 100 ppm.

[b] Insoluble

## DETERMINATION OF LEAD

The literature abounds with methods for the determination of lead. This reflects the long-standing interest in the development of more rapid and selective methods for this element in a great variety of matrices. In general these methods involve a separation step in which lead is removed from interferences and concentrated. Solvent extraction using sodium diethyldithiocarbamate or dithizone followed by photometric determination of the resulting lead complex in the organic phase has proven sensitive and selective (30-32). However, extraction methods often require addition of a number of reagents which require painstaking purification. The high pH values necessary for selectivity often precludes analysis of samples high in metal content and can lead to reagent instability. Ion exchange methods have enabled separation of lead from bismuth, cadmium, and thallium, which often interfere with extraction techniques, as well as from a large number of other metals (1). Using strong-base anion exchange resin, separation from at least thirty-nine ions can be effected in hydrochloric acid media (5). This is the basis for several methods utilizing subsequent polarographic, spectrophotometric, and spectroscopic determinations (33-36). Again much sample manipulation is involved, consuming time and sacrificing accuracy.

This section describes application of forced-flow anion exchange chromatography to the determination of lead in complex matrices. In a manner similar to that used for iron(III), lead(II) is sorbed to an anion exchange column from dilute hydrochloric acid and separated from most matrix elements. It is then eluted with more concentrated acid and estimated spectrophotometrically from the height of its elution peak. The method is rapid and nearly specific; accuracy compares favorably with other methods for small amounts of lead.

## Experimental

Apparatus. The chromatograph was as previously described.

Reagents. Dowex 1-X8, 200-400 mesh, Bio-Rad Laboratories, capacity 3.2 meq/g of dry resin was used for the analytical separations. The resin was washed with methanol, concentrated hydrochloric acid, dilute hydrochloric acid and finally acetone prior to air drying. The beads were then immediately sieved isolating the 250-325 fraction. Extreme fines not separated after sieving were removed by methanol flotation.

The resins used in the determination of HETP values, Amberlite IRA-900 and IRA-400 and Amberlyst A-26 were obtained from Rohm and Haas. Dowex 1-X8 20-50 mesh, from J. T. Baker Chemical Company was used. After washing in methanol the resins were subsequently washed in water, 0.5M hydrochloric acid, and again in water. The excess moisture was removed using paper towels prior to grinding to the desired water moist mesh size. The gel-type resins Amberlite IRA-400 and

Dowex 1-X8 were ground in a Model 4-E Quaker City Mill. The macroreticular resins, IRA-900 and A-26 fouled the mill and were hand ground using a mortar and pestle. The resins were then repeatedly sieved retaining the respective 150-200 mesh fractions. Again extreme fines were removed by methanol flotation.

The resin used in packing the analytical column was dried prior to weighing. The beads, prepared as described above, were again washed with acetone and air dried. The resin was then stored in a desiccator under vacuum over anhydrous calcium sulfate for at least 24 hr before weighing.

Samples. The alloys analyzed were standard reference materials obtained from the National Bureau of Standards. The samples were thoroughly mixed before weighing. Each weighed sample was then transferred to an Erlenmeyer flask and covered with 30% hydrogen peroxide solution. A small amount of concentrated hydrochloric acid was then added (1-3 ml) and a watch glass immediately placed on the flask. The samples rapidly dissolved without heating. Excess hydrogen peroxide was driven off by heating to near dryness. A measured amount of concentrated hydrochloric acid was then added such that, upon rinsing and subsequent dilution with water into a volumetric flask, the solution was made to 0.5$\underline{M}$ HCl. Chemicals employed were reagent grade. It was necessary to analyze Standard Sample 54D (Tin-Base Bearing Metal) soon after dilution to prevent hydrolysis.

Reagent Grade lead; assay 100.0%, as obtained from J. T. Baker Chemical Company, was used to obtain the analytical calibration plot. The lead was dissolved using the same procedure used for the reference materials.

All solutions and eluents were prepared from reagent grade hydrochloric acid and distilled, deionized water.

Column Preparation. In all cases a Chromatronix Model LC-6M-13 column (6.35 mm i.d.) was used. Two outlet plungers were employed to obtain the bed height desired for the lead analyses. The analytical column was prepared by adding 1.000 g resin in a thick aqueous slurry to a column with one plunger in place. While the resin settled flow was maintained by applying suction at the column outlet with a syringe. After settling, the bed was compressed as the other plunger was inserted. The column was then installed in the chromatograph and the flow reversed followed again by compression at both ends. This process of reversing the column, forcing a rapid flow of water, and compressing was continued until no further shrinkage was obtained. This yielded a bed length of 7.25 cm.

The columns used in obtaining plate height data were packed in similar fashion. Resin was added to yield a bed length of approximately 10 cm. This column packing technique should only be employed with short columns to prevent nonuniformity in bed density.

Procedures. For the analysis of lead in alloys the standard reference materials, after dissolution as described, were diluted with 0.5M HCl to a concentration of from 0.4 to 40 µg Pb/ml (for optimum precision 10 to 30 µg Pb/ml). The pressure was adjusted to give a flow rate in sorbing eluent (0.5M HCl) of 3.0 ml/min with the sample valve in the "Inject" position and the 7.25-cm column of Dowex 1-X8 in place. The valve was returned and the 0.969 ml sample loop was filled using a 3-ml syringe to insure adequate purging of any previous sample. The detector was set at 270 nm. After allowing 2 min for column pre-equilibration the sample was injected. After 1 min the eluent was switched from 0.5M HCl to 8.0M HCl. During this first minute most of the nonsorbing matrix was removed. The elution with 8.0M HCl was continued until 6 min after injection, during which time the remainder of the matrix was removed followed by elution of lead. The eluent was then changed to 0.5M HCl to prepare the column for the next sample. The recorded peak height (in absorbance) was directly proportional to the lead content in the sample. For optimum accuracy a calibration curve was constructed by running standard solutions alternately with unknown samples using the same procedure.

To analyze for extractable lead in glazed pottery the unit was first washed with detergent and rinsed thoroughly with distilled water. The unit was then dried and filled to 75% capacity with 4% acetic acid. The unit was covered with a watch glass and allowed to stand 24 hr at room temperature. The sample was then thoroughly mixed and a 25-ml aliquot taken. The aliquot was taken to near dryness in a 250-ml Erlenmeyer flask. Two drops of concentrated hydrochloric acid were added and the sample taken to dryness but not baked. The sample was diluted to 25 ml with 0.5M HCl and analyzed using the same elution sequence as was used for the alloys.

## Results and Discussion

Choice of Method. This method takes advantage of two noteworthy properties of lead in solutions of hydrochloric acid to achieve exceptional selectivity and good sensitivity. Lead displays strong ultraviolet absorption at 272 nm having a molar absorptivity of 15,500 in 8M HCl. This peak is sharp with its maximum unshifted with small changes in acid concentration, as is shown in Figure 13. Although 37 of the 70 metal ions surveyed display sufficient ultraviolet absorption in hydrochloric acid to be detected, few have an appreciable molar absorptivity at this wavelength. The second important property of lead is its ability to be sorbed to anion exchange resins from low concentrations of hydrochloric acid and eluted at higher concentrations. Only silver(I) and rhodium(III) share this property. The dual selectivity of sorption at 0.5M HCl, desorption at 8.0M HCl and monitoring at or around 272 nm makes this a nearly specific method for lead.

Choice of Resin. Four resins were compared for efficiency of separation by determining the HETP for a 42-μl sample

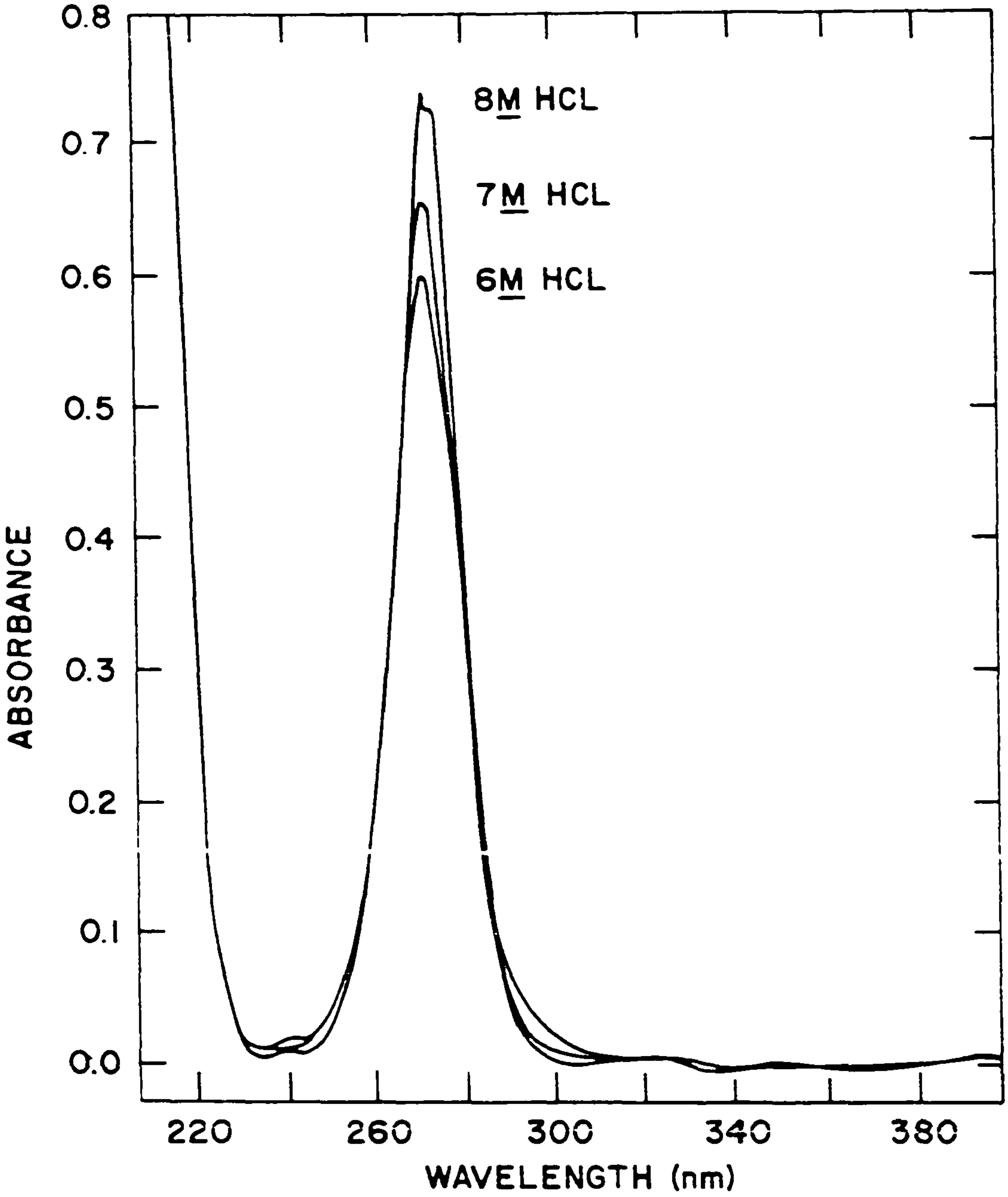

Figure 13. Spectra of 10 μg Pb(II)/ml in hydrochloric acid

containing 0.1 μmole of lead(II) at various flow rates of 1.0M HCl. These data are shown in Figure 14. This concentration of acid was chosen to ensure an accurately measurable retention volume on the four resins employed and to provide sufficient absorbance for detection. The resins were all ground and sieved water moist in the chloride form to ensure uniformity in particle size in making this comparison. As is indicated in Figure 14, Dowex 1-X8 displayed the lowest HETP values at any given flow rate. Also, the resulting linear plot of HETP versus flow rate exhibited the smallest slope, making this the resin of choice at high flow velocities. In general the peak shapes observed were more symmetrical for Dowex 1-X8 than for the other resins. The volume distribution ratios for lead in 1.0M HCl on Dowex 1-X8, IRA-400, IRA-900, and A-26 were 13.2, 14.8, 12.4, and 10.2, respectively.

Choice of Conditions. Although maximum retention of lead on Dowex 1-X8 is obtained at 1.3M HCl, 0.5M HCl was chosen as the sorbing eluent to obtain greater resolution from ions partitioning at low acid concentrations. Figure 15 shows the distribution ratios of four metals likely to interfere with this method. These values were obtained from column retention volumes, assuming 70% packing efficiency. Although antimony (V) and rhodium(III) are also likely to cause interference, suitable retention values could not be obtained at low acid concentrations. Inspection of these data show that a separa-

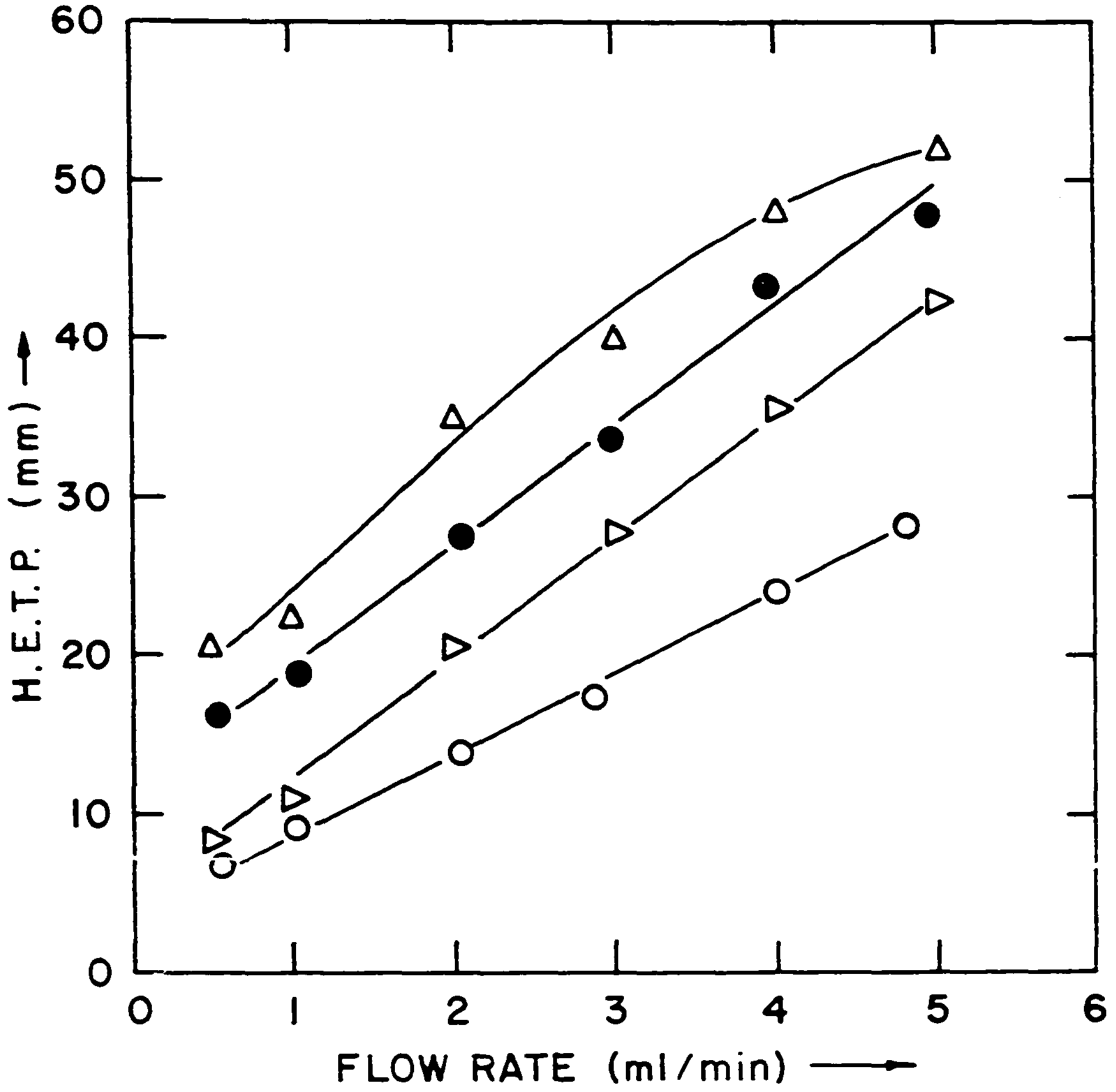

Figure 14. Height equivalent to a theoretical plate vs. flow rate

● Amberlite IRA-400

△ Amberlite IRA-900

▷ Amberlyst A-26

○ Dowex 1-X8

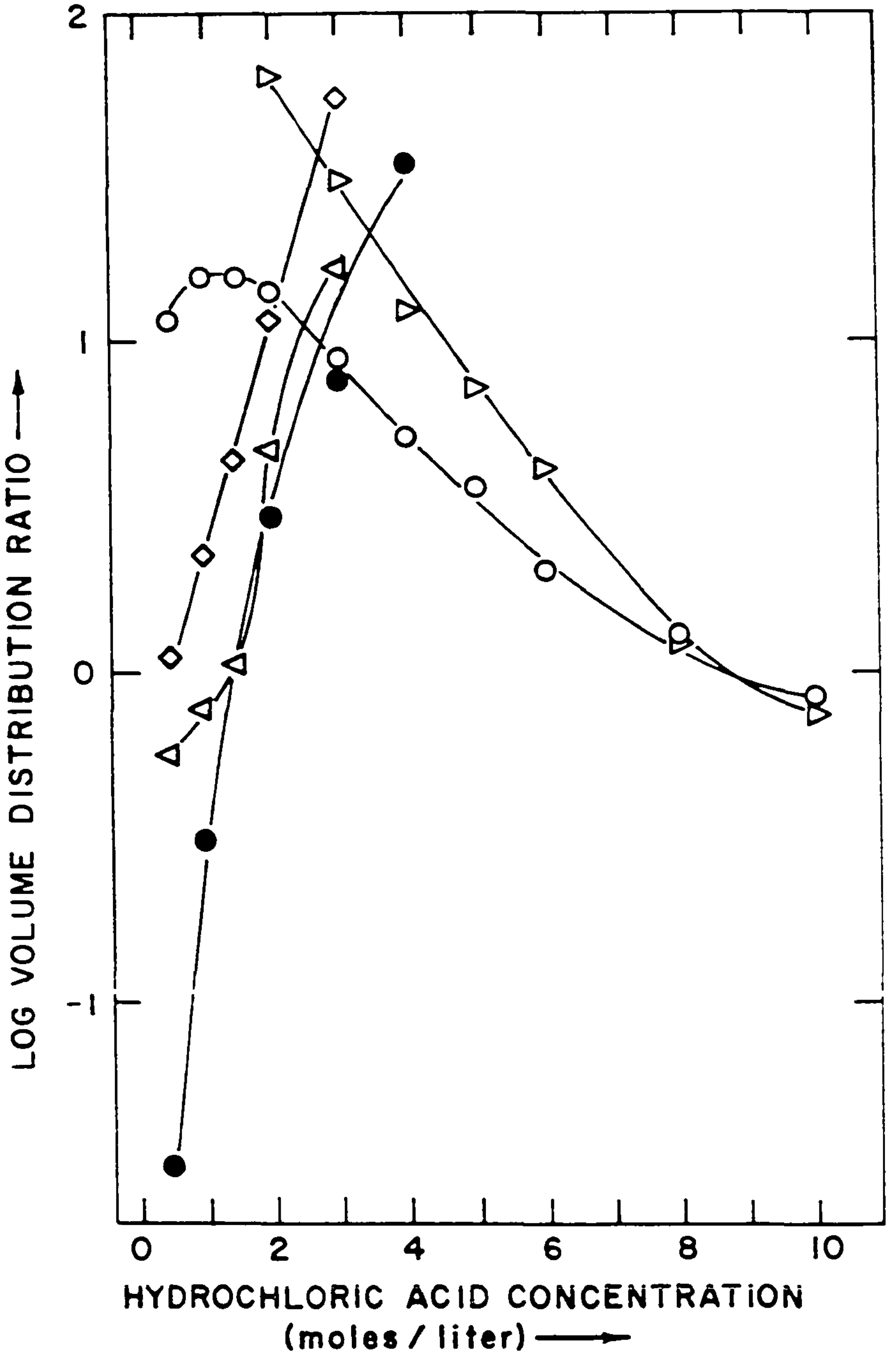

Figure 15. Distribution ratio vs. hydrochloric acid concentration

● Iron(III)
○ Lead(II)
◇ Molybdenum(VI)
▷ Silver(I)
◁ Uranium(VI)

tion factor of about 10 can be achieved for molybdenum(VI) at 0.5M HCl, and an even greater separation factor for all other ions (with exception of rhodium(III)). Lead, however, is still retained at this concentration. The choice of eluent for removal of lead from the column was dictated by the need for resolving the peak maximum from the solvent change signal which is shown with a typical elution curve in Figure 16. Although higher hydrochloric acid concentrations would remove lead more rapidly, 8M HCl was chosen to allow a base line of zero under the peak maximum.

Column length was a compromise between time, resolution and sensitivity. The 7.25-cm column employed allows rapid separation from moderate amounts of molybdenum and other elements at flow rates up to 3.0 ml/min. For greater resolution from slightly partitioning elements, slower flow rates or increased column length can be employed. The flow rate of 3.0 ml/min corresponds to an elution sequence of 8 min from injection to injection. The sequence for this column varies from 17 min at a flow rate of 0.5M HCl of 1 ml/min to 5 min at 5 ml/min. This corresponds to a 44% decrease in detector response at the elution maximum. As both peak area and peak height are a function of flow rate, it must be carefully controlled for best results.

The choice of sample loop size was again a compromise. Larger loop sizes can be used for greater sensitivity, however, unless the column length is greatly increased separation from

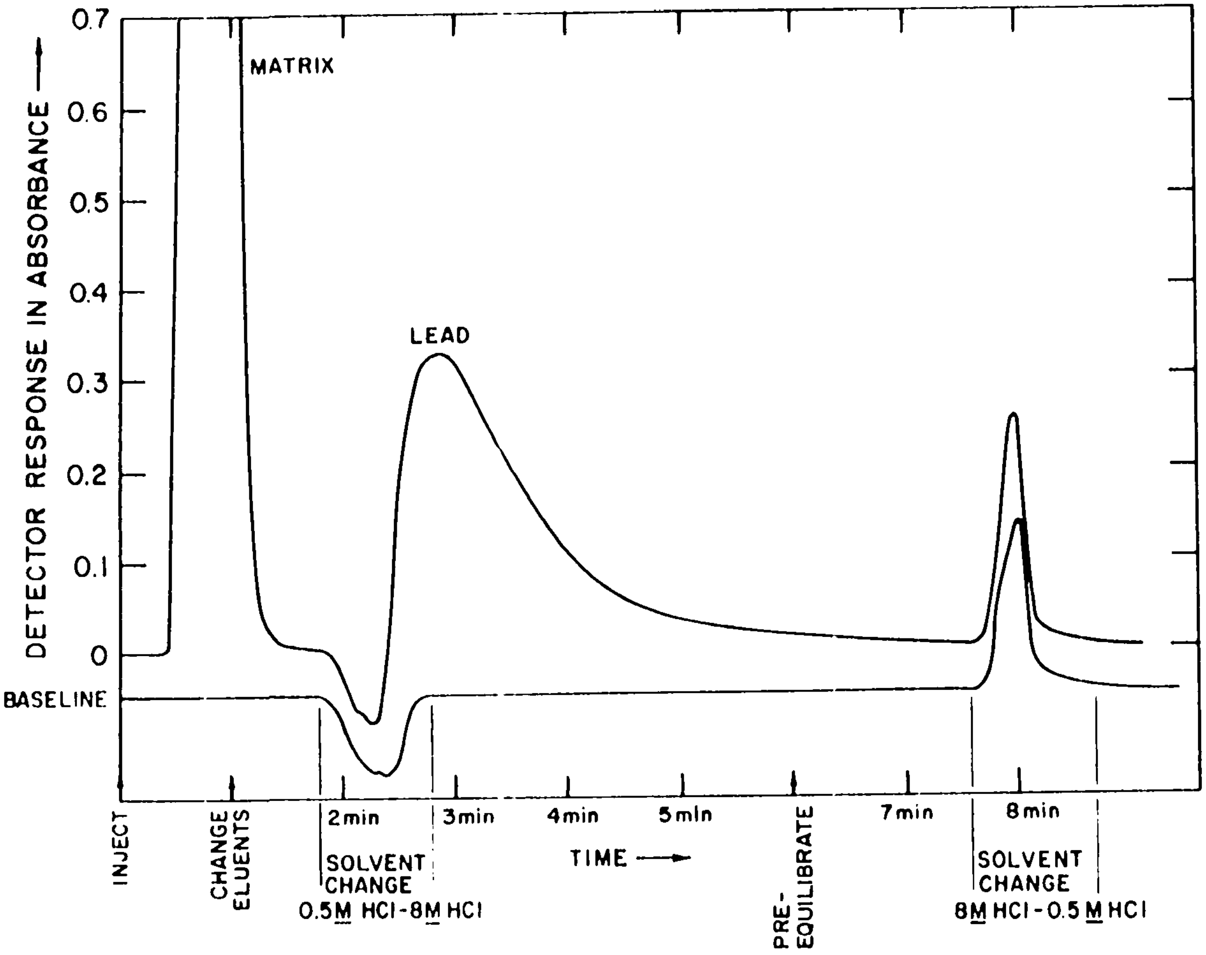

Figure 16. Typical chromatogram of lead analysis

Conditions: Sample, NBS 37d 163 mg/100 ml; sample volume, 0.969 ml; flow rate of 0.5M HCl, 3.0 ml/min; detection at 270 nm interfering ions is not possible. For example, if the sample volume is increased to 10 ml, resolution of iron and lead can barely be achieved on a 17-cm column at 2.0 ml/min, although the separation factor for lead/iron in 0.5M HCl is nearly 80.

Since the sample loop volume is only approximately proportional to the length of tubing installed, unit volumes are not easily obtained. The dimension of the 0.969 ml loop reported has no special significance.

Accuracy and Precision. Data on accuracy and precision in the analysis of standard reference materials are given in Table II. These data were obtained using a single injection of each of three weighings. The calibration curve was constructed from a single injection of each of three standard solutions run alternately with the samples. A linear least squares data fit was used to obtain the lead content of the unknowns using a programmable calculator. Graphical methods yielded the same results. As spectrophotometric detection is employed using no attenuation, precision depends on sample concentration. Concentrations from 0.4 to 40 μg Pb/ml can be detected corresponding to absorbance values of 0.01 and 1.0 or 1% and 100% of the recorder scale. Optimum results were obtained from 10 to 30 μg Pb/ml or in an absorbance range of from 0.222 to 0.647. The relative standard deviation on a single weighing of NBS 124d at the center of this range was 0.23 pph.

A variety of pottery pieces were analyzed for extractable

Table II. Analysis of NBS Samples for Lead

| Sample type | NBS No. | NBS analysis | Our analysis | Mean error | Rel std dev, pph |
|---|---|---|---|---|---|
| Lead-base bearing metal | 53B | 84.4% | 85.0% | +0.7% | 1.34 |
| Ounce metal | 124d | 5.20% | 5.18% | -0.4% | 0.95 |
| Sheet brass | 37D | 0.94% | 0.95% | +1.1% | 1.05 |
| Tin-base bearing metal | 54D | 0.62% | 0.61% | -1.6% | 1.64 |
| Manganese bronze | 62B | 0.28% | 0.28% | 0% | 0.0 |

lead. Lead was detected in the leaching solutions from two of the twelve units at levels of 0.4 and 1.4 μg Pb/ml. Standards were treated using the procedure described and a relative standard deviation of 1.6 pph was obtained at 7 μg/ml.

There are two kinds of interference common to this type of analysis. Column overloading can cause alteration of peak shape and retention time and hence a dependency of peak height on matrix composition. However, even in the analysis of tin-base bearing metal, where the tin matrix is tightly sorbed to the column while present in a 143 to 1 ratio to lead, no interference was noted. This was due to the small fraction of the column capacity occupied by the tin even after repeated analyses.

The other type of interference is due to ions that are retained in 0.5<u>M</u> HCl stripped in 8.0<u>M</u> HCl and absorb at 270 nm. Of the cations tested only three were found to interfere. Rhodium(III), antimony(V) and molybdenum(VI) were found to cause a 1% error in the analysis with metal/lead ratios of 0.009, 0.181, and 5.30 respectively. Greater resolution from molybdenum can be achieved as previously mentioned. Antimony can be removed during sample dissolution by volatilization. Rhodium(III) can be oxidized to the tetravalent state which will not be eluted with lead.

Nitrate ion can also cause error and should be driven off by taking the sample to dryness in concentrated hydrochloric acid prior to analysis.

# DETERMINATION OF METALS IN MIXED HYDROCHLORIC AND PERCHLORIC ACIDS

Although hydrochloric acid has proven the most useful medium for separation of heavy metals, strong adsorption of a few metals which resist rapid elution at any acid concentration is a serious limitation to use of this system. Mixtures of hydrochloric and hydrofluoric acids have been employed to elute sequentially some of these elements (12). However, there remains a need for a more versatile separation medium that is chemically compatible with the hydrochloric acid system.

This section describes a new solvent system, a gradient mixture of 10$\underline{M}$ HCl and 5$\underline{M}$ $HClO_4$. This not only enables elution of metals strongly retained on chloride-form anion exchange resins but also makes possible several useful separations of these ions. In addition it enables detection of these elements via the ultraviolet absorption of their chloride complexes. Quantitative analysis of a multicomponent sample is illustrated.

## Experimental

Apparatus. The chromatograph was as previously described.

Resin. Amberlyst A-26 macroreticular strong-base anion exchange resin was obtained from Rohm and Haas Company. In the chloride form the capacity is about 4.1-4.4 meq/gram dry or 0.95-1.1 meq/ml.

The resin was washed in dilute hydrochloric acid, concentrated hydrochloric acid, methanol, and water prior to grinding water moist with mortar and pestle. The resin was sieved before drying and the 150-200 mesh fraction retained. Extreme fines were removed by methanol flotation.

Before weighing, the resin used in column separations was rinsed with acetone, air dried, and finally dried under vacuum over anhydrous calcium sulfate for 24 hr.

For batch distribution studies a portion of the resin, prepared as described, was placed in a column and washed with 5M perchloric acid until the effluent was optically transparent in the ultraviolet. This serves to leach organic impurities as well as effect complete conversion to the perchlorate form. The resin, after washing with deionized water until the column effluent reached pH 6, was air dried before weighing.

Reagents. Except for platinum(IV) prepared from the metal, all metal ion solutions were prepared by dissolving reagent grade oxides or chlorides in either 6M HCl or a mixture of 0.2M HCl-4.9M $HClO_4$. From these stock solutions dilutions were made adding 70% perchloric acid, concentrated hydrochloric acid, and distilled, deionized water in appropriate amounts to match the eluent and sample compositions. Chromium(VI) was first dissolved in dilute perchloric acid or water. Hydrochloric acid was added immediately before injection to prevent reduction to chromium(III). Ruthenium(IV) was prepared by storing a solution of the commercial "Trichloride" in 6$\underline{M}$ HCl under air for a year. After dilution, ruthenium(IV) and tin(IV) were allowed to stand 10 hours prior to injection. For column retention studies the metal concentrations in the injected solutions ranged from 100 μg/ml to 0.1 μg/ml depending upon sensitivity of detection. For the analytical separations concentrations from 40-10,000 μg/ml were employed.

For batch equilibrations mercuric oxide was dissolved in measured amounts of perchloric or perchloric and hydrochloric acids. The acidity was then adjusted by addition of sodium hydroxide and diluted to volume. The mercury(II) concentration was 0.0200$\underline{M}$.

Column Preparation. In changing from the chloride to the perchlorate form strong-base anion exchange resins shrink markedly (37). To prevent continual change of column length and bed density when changing eluents, a special packing procedure is used. A Chromatronix LC-6M-13 column (6.35 mm i.d.) is packed in a vertical position with one of two outlet plungers in place. A thick aqueous slurry of chloride-form resin is added and allowed to settle while maintaining a constant flow by applying suction at the column outlet. The other plunger is inserted and the column compressed. The column is then installed in the chromatograph and treated with water, 3$\underline{M}$ $HClO_4$, water, 3$\underline{M}$ HCl and water in 10 ml portions. The column is then reversed, both ends compressed, and the procedure repeated. This is continued for 10-15 cycles or until the bed no longer pulls away from the inlet plunger after conversion to the perchlorate form. This procedure was employed for the 9.15-cm, 3.80-cm, and 1.85-cm columns employed containing 1.072 g, 0.400 g and 0.241 g dry chloride-form resin, respectively. Shrinkage data for the 9.15-cm (final length) column are shown in Figure 17.

Distribution Ratios. Distribution ratios of metal ions with A-26 resin were determined from recorded column elution curves. The detector was set at 225 nm and the flow rate was adjusted to between 0.5 and 1.0 ml/min for the 9.15-cm column or from 1.0 to 2.0 ml/min for the 1.85-cm column. The sample was injected using a 50-μl sample loop and the elution curve (in absorbance) recorded. Nickel(II) was used as the reference ion because it has a retention volume of zero at all concentrations but has UV absorption sufficient for detection. The weight distribution ratio is then calculated:

$$D_w = \frac{\text{(Retention Volume Metal Ion)-(Retention Volume Nickel)}}{\text{(Weight of Resin in Column)}}$$

Using the graduated eluent collector and event marker, direct calibration of the recorded peak is possible in 100-μl divisions allowing estimation of retention volumes to ± 20 μl. Distribution ratios from $10^{-2}$ to $10^{2}$ can be determined using the 9.15-cm column, but best results were obtained for values from 0.1 to 10. To shorten the time required to elute strongly sorbed ions, the 1.85-cm column was used to determine

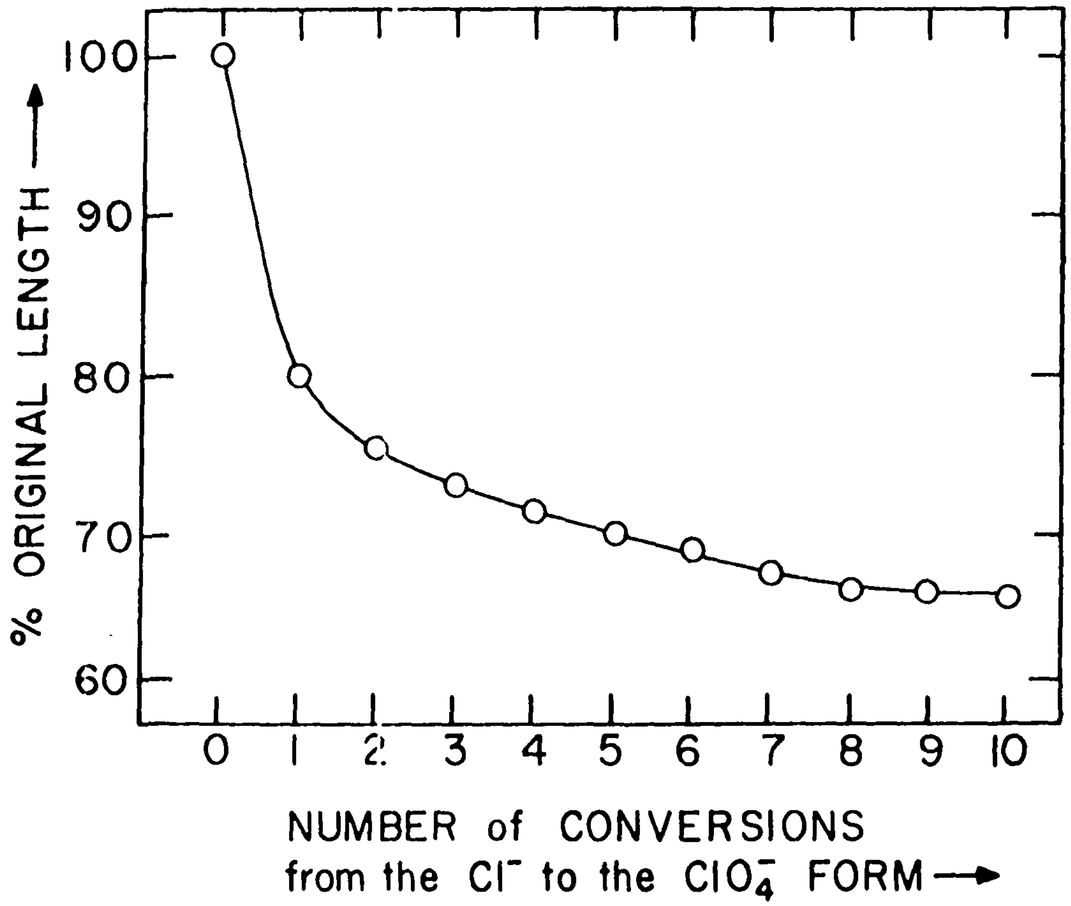

Figure 17. Shrinkage data for a column of Amberlyst A-26 anion exchange resin

approximate values for distribution ratios greater than 50.

Weight distribution ratios for mercury(II) were determined after batch equilibration of 10 ml of solution with 1.000 g of resin for 1 hr.

A 5-ml aliquot of the aqueous phase was made to pH 6 with sodium hydroxide and sodium acetate, excess EDTA was added, and mercury(II) determined by back titration with zinc(II) using NAS as the indicator (38).

Separations. All separations were monitored at 225 nm. The 50-µl sample loop was used. Separation of nickel(II), palladium(II), and platinum(IV) and separation of arsenic(III), antimony(III) and bismuth(III) were accomplished on the 9.15-cm column with an initial flow rate of 1.0 ml/min. The 3.80-cm column with a flow rate of 0.86 ml/min was used to separate lead(II), copper(II), iron(III), mercury(II) and tin(IV).

The pressure is adjusted to yield the appropriate flow rate and the sample is injected. Eluents are changed in a time sequence, compensating for the volume between eluent manifold and detector.

## Results

Distribution ratios for metal ions in hydrochloric acid-perchloric acid mixtures are given in Table III. The distribution ratio for several metal ions decreases in regular fashion with increasing perchloric and decreasing hydrochloric acid concentrations. The curves for some of the metal ions pass

Table III. Anion Exchange Weight Distribution Ratios in a Gradient Mixture of 10M HCl and 5M $HClO_4$

| $[\mathrm{HCl}]$, $[\mathrm{HClO_4}]$ | Sb(III) | Bi(III) | Cr(VI) | Au(III) | Hg(II) | Pd(II) | Pt(IV) | Ru(IV) | Tl(III) | Sn(IV) |
|---|---|---|---|---|---|---|---|---|---|---|
| 10.0M, 0.0M | ~71 | ~93 | 1.66 | >250 | ~150 | ~ 56 | >166 | 3.82 | >200 | >200 |
| 9.0M, 0.5M | 21.6 | 18.6 | 0.61 | >250 | 34.4 | 12.2 | >166 | 1.68 | ~ 83 | >200 |
| 8.0M, 1.0M | 11.0 | 6.44 | 0.29 | >250 | 17.2 | 5.24 | ~ 96 | 0.90 | ~ 69 | >200 |
| 7.0M, 1.5M | 7.23 | 3.14 | 0.25 | >250 | 9.79 | 3.05 | ~ 40 | 0.47 | ~ 67 | >200 |
| 6.0M, 2.0M | 5.68 | 1.95 | 0.20 | >250 | 6.92 | 2.14 | 41.0 | 0.34 | ~ 75 | ~200 |
| 5.0M, 2.5M | 4.50 | 1.17 | 0.20 | >250 | 4.36 | 1.41 | 24.3 | 0.19 | ~ 65 | ~110 |
| 4.0M, 3.0M | 4.38 | 0.87 | 0.23 | >250 | 3.54 | 1.12 | 17.9 | 0.11 | ~ 62 | ~ 67 |
| 3.0M, 3.5M | 4.54 | 0.72 | 0.21 | >250 | 2.89 | 0.85 | 13.0 | ~ 0 | ~ 60 | ~ 47 |
| 2.0M, 4.0M | 5.42 | 0.60 | 0.23 | >250 | 2.43 | 0.74 | 11.1 | ~ 0 | ~ 97 | 47.6 |
| 1.0M, 4.5M | 8.30 | 0.53 | 0.15 | ~200 | 1.92 | 0.62 | 9.01 | ~ 0 | ~150 | 29.3 |
| 0.6M, 4.7M | 11.1 | 0.72 | 0.17 | ~200 | 1.94 | 0.45 | 7.85 | —— | ~170 | 22.4 |
| 0.2M, 4.9M | 16.3 | 1.88 | 0.02 | ~200 | 2.28 | 0.35 | 7.10 | —— | ~110 | 13.2 |
| 0.0M, 5.0M | 3.64 | 7.81 | 0.02 | ~190 | 4.31 | 0.56 | 7.12 | —— | ~170 | 1.66 |

through minima, as illustrated by mercury(II), antimony(III), bismuth(III) and thallium(III) in Figure 18. With the exception of gold(III) and thallium(III), incorporation of perchloric acid in the eluent lowers the distribution ratios of all metal ions studied sufficiently to permit their elution from an anion exchange column.

Examination of Table III shows sufficient differences in distribution ratios in the hydrochloric-perchloric acid system to permit a number of column separations of metal ion mixtures. Also, conventional anion exchange separations based on variation in hydrochloric acid concentration alone are still possible. In either system many metal ions form chloride complexes which absorb strongly in the UV, thus automatic detection and recording of eluted metal peaks is feasible. The separations described below were carried out to demonstrate the utility and rapidity of anion exchange separations using the hydrochloric-perchloric acid system using a forced-flow liquid chromatograph.

The separation of arsenic(III), antimony(III) and bismuth (III) was carried out and automatically recorded, as shown in Figure 19. Arsenic(III) is eluted with 4$\underline{M}$ hydrochloric acid and the other two metal ions are strongly retained by the column. Upon switching to 1$\underline{M}$ HCl-4.5$\underline{M}$ $HClO_4$, bismuth ($D_w$ = 0.53) is rapidly eluted and is separated from the following elution peak for antimony ($D_w$ = 8.30). The negative peak and

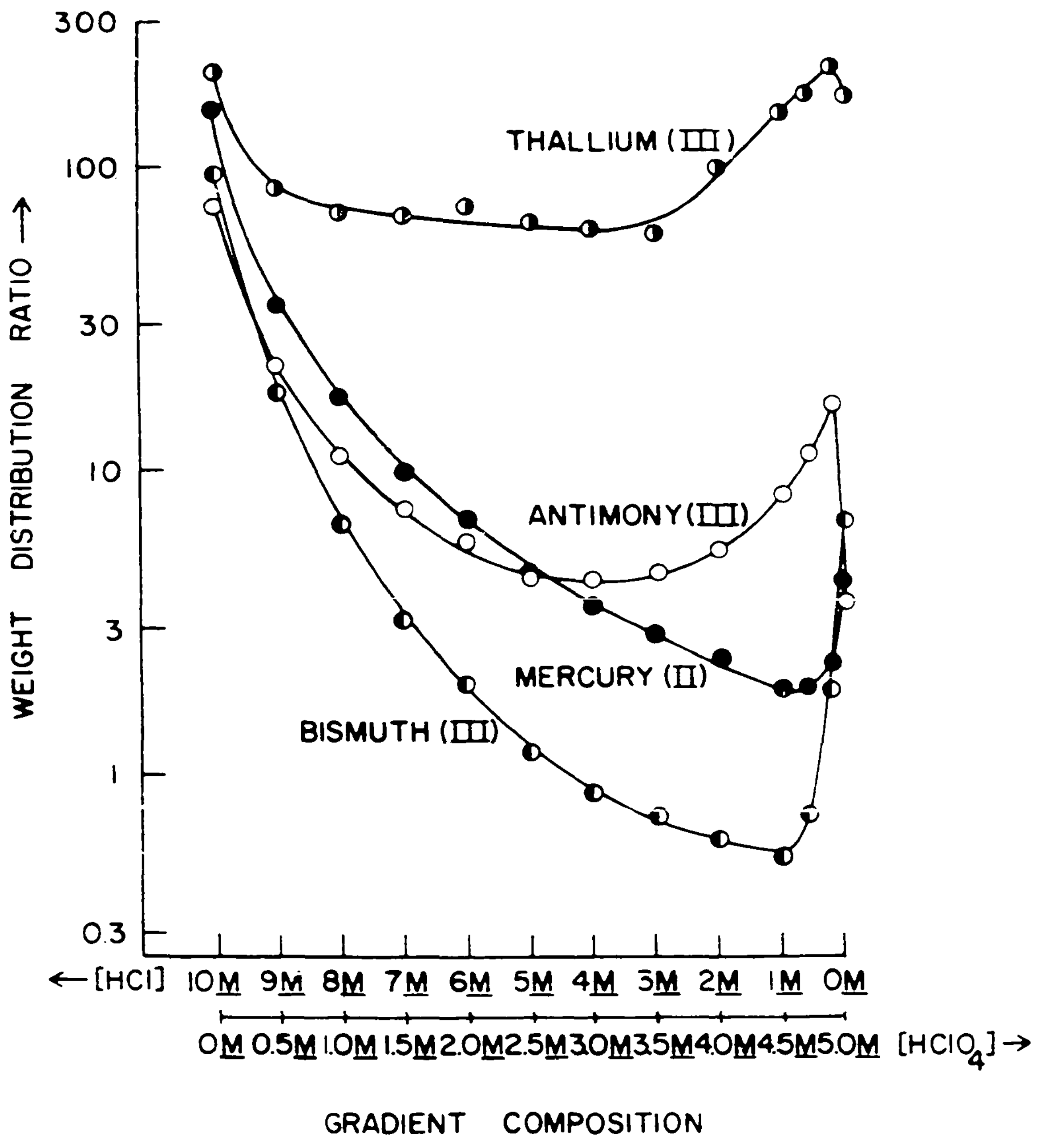

Figure 18. Distribution ratios for ions displaying minima

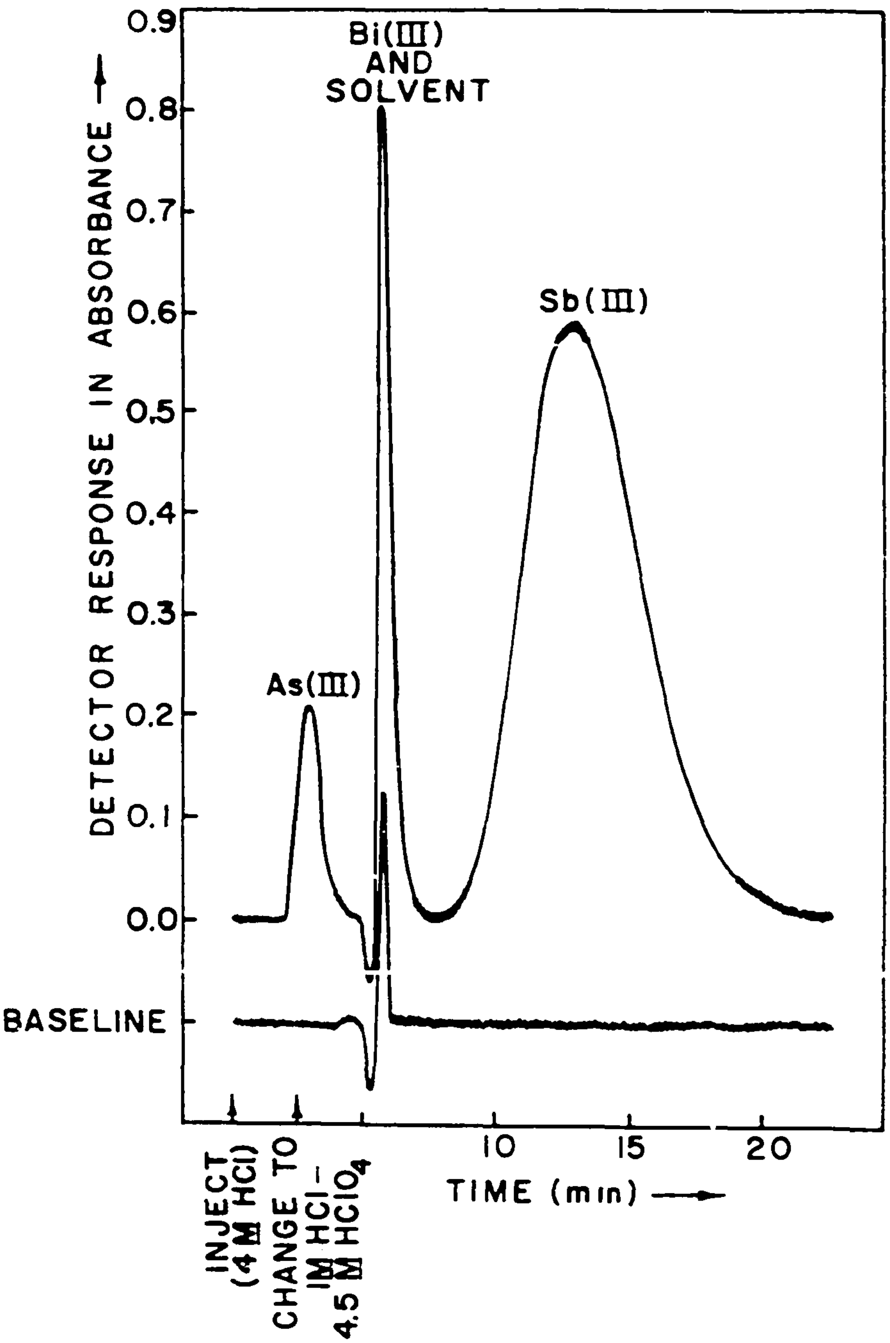

Figure 19. Separation of 50 μg arsenic(III), 2.5 μg bismuth (III), and 250 μg antimony(III)

Conditions: Resin, Amberlyst A-26; column, 9.15 cm x 0.63 cm i.d.; sample volume, 50 μl; flow rate of 4<u>M</u> HCl, 1.0 ml/min; detection wavelength, 225 nm the following positive peak in the baseline curve result from the change in eluent.

The separation of nickel(II), palladium(II) and platinum(IV) is shown in Figure 20. Although nickel(II) is separated from the other two by elution with 6$\underline{M}$ hydrochloric acid alone, palladium(II) and platinum(IV) must be separated from each other using the hydrochloric-perchloric acid system. Again, a baseline peak is observed which results from a change in eluent composition.

More complicated separations can be achieved, as illustrated by the separation of five elements recorded in Figure 21. Here, lead(II) is eluted with 8$\underline{M}$ hydrochloric acid and the other elements are held by the column. Before the lead (II) is completely eluted, the eluent is changed to 4$\underline{M}$ HCl to complete elution of the lead and to elute copper(II). Iron (III) is eluted with 1$\underline{M}$ HCl, mercury(II) with 4$\underline{M}$ HCl-3$\underline{M}$ $HClO_4$, and finally tin(IV) is removed from the column with 0.1$\underline{M}$ HCl-5.95$\underline{M}$ $HClO_4$. The entire separation is complete in only 25 min.

Although the separations cited are complete, quantitative analysis of mixtures also depends on the ability to relate reproducibly peak height (or peak area) to the amount of a particular metal. Figure 22 shows calibration curves for four of the five metal ions separated in Figure 21. For mixtures of this type it is necessary to separate the detector response from UV absorption of the eluted ion from the response caused by a change in eluent composition. In Figure 21 the sharp

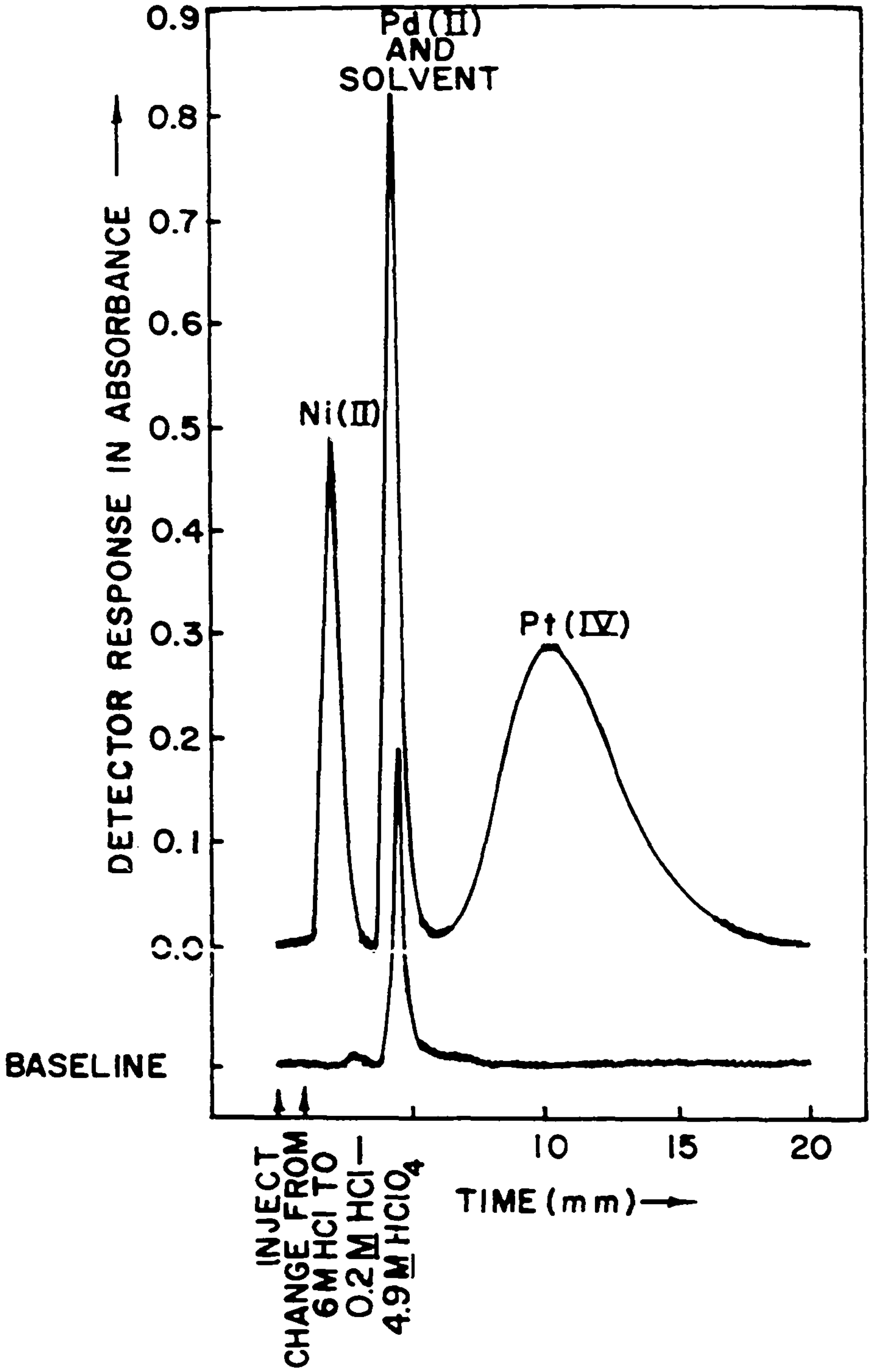

Figure 20. Separation of 500 μg nickel(II), 2 μg palladium (II), and 50 μg platinum(IV)

Conditions: Resin, Amberlyst A-26; column, 9.15 cm x 0.63 cm i.d.; sample volume, 50 μl; flow rate of 6M HCl, 1.0 ml/min; detection wavelength, 225 nm

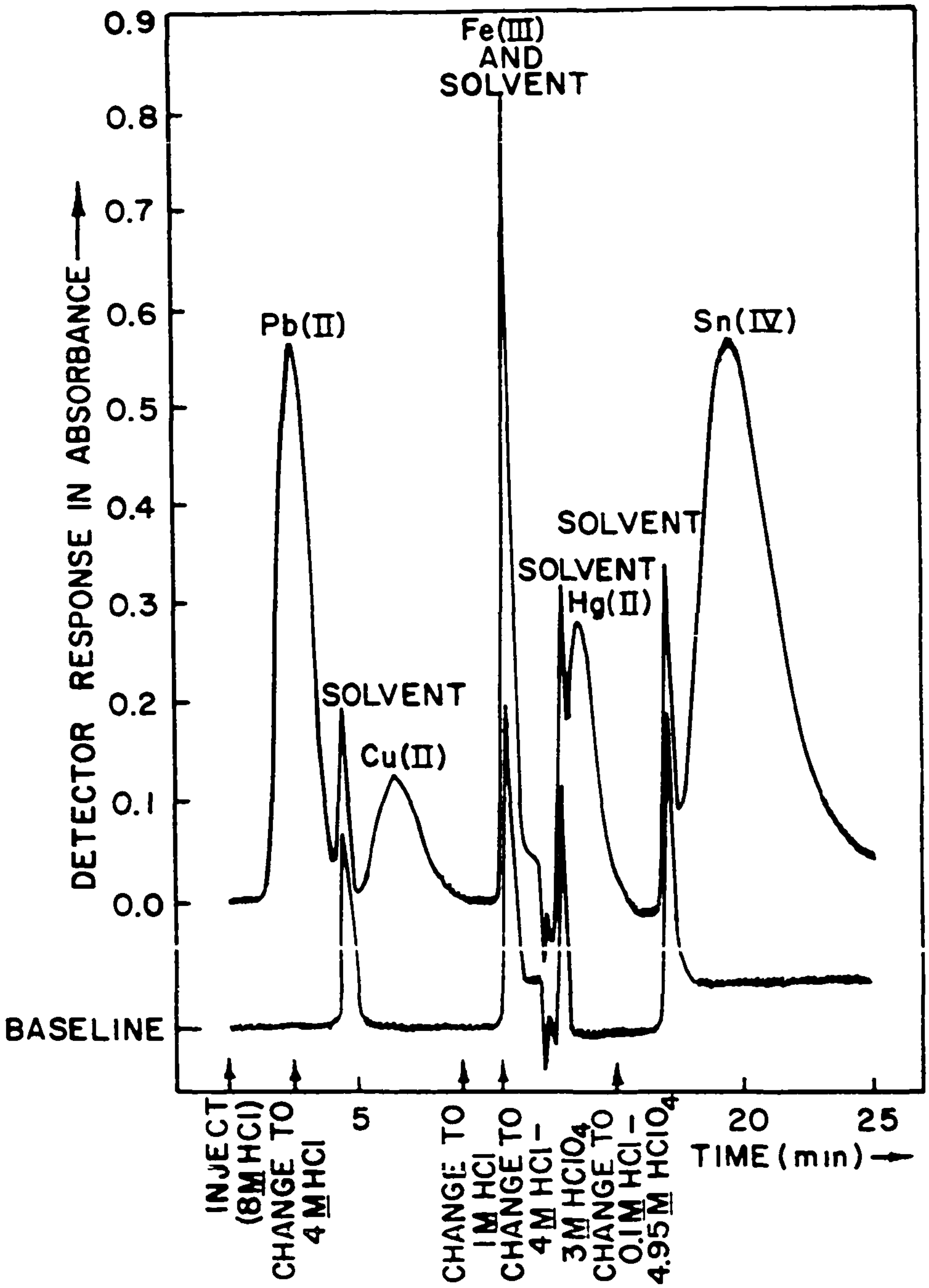

Figure 21. Separation of 70 μg lead(II), 17.5 μg copper(II), 3.5 μg iron(III), 3.5 μg mercury(II), and 105 μg tin(IV)
Conditions: Resin, Amberlyst A-26; column, 3.80 cm x 0.63 cm i.d.; sample volume, 50 μl; flow rate of 8$\underline{M}$ HCl, 0.86 ml/min; detection wavelength, 225 nm

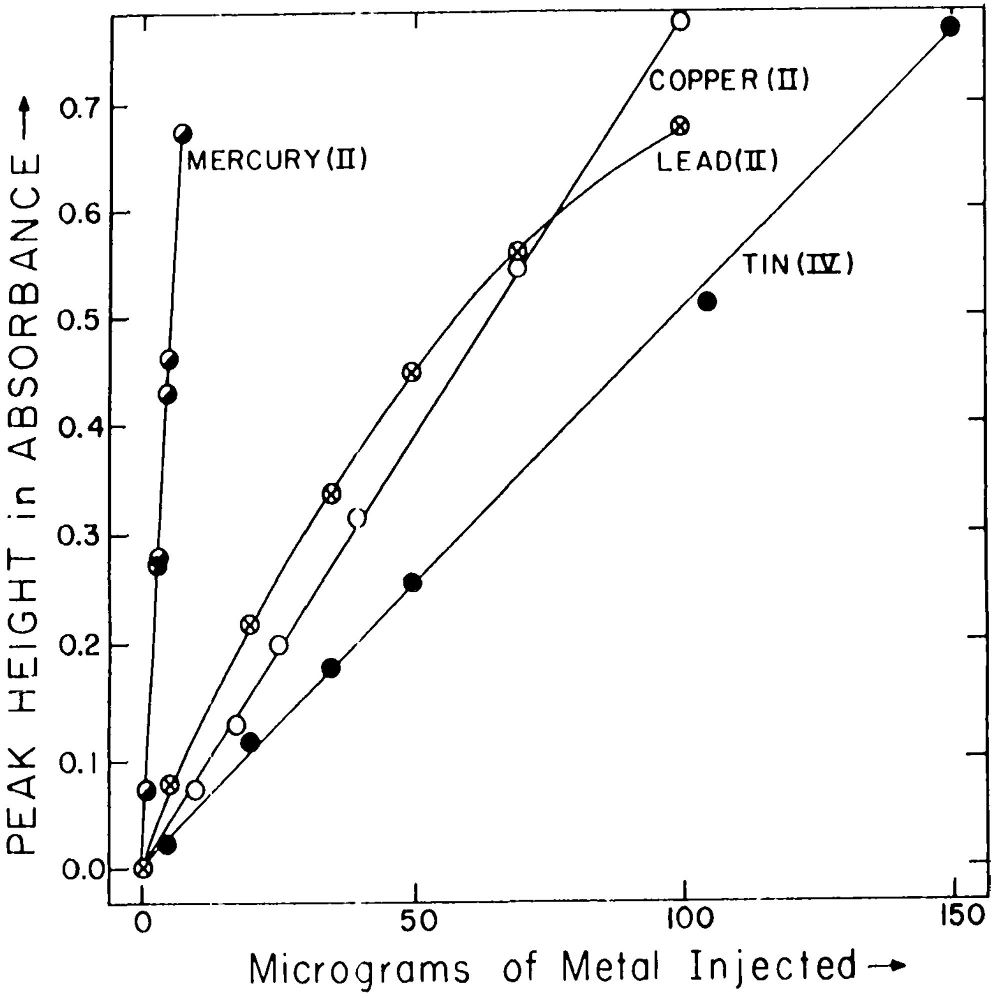

Figure 22. Calibration plots for four metals of a five metal mixture

baseline peak precludes quantitative determination of iron (III). The baseline peak near mercury(II) causes no difficulty provided peak height, rather than peak area, is used for the quantitation. Similarly, the baseline solvent peaks do not interfere at all with the lead, copper, or tin peaks.

The calibration plots in Figure 22 were prepared by separating successive dilutions of two solutions containing varied proportions of these five metal ions. These plots are linear except for lead(II). A curved plot is common for metals that are not taken up by the resin under the sample injection conditions. Lead(II) has a linear calibration curve if it is first sorbed at 0.5M hydrochloric acid and later stripped with 8M acid (39).

The sensitivity of detection varies because of differences in molar absorptivity of various metal complexes and because a fixed-wavelength (225 nm) is used for all elements. The sensitivity may be diminished in some cases where a baseline solvent peak coincides with a metal peak and elution conditions must be altered to effect resolution of the two. However, the strong adsorption of some of these ions from hydrochloric acid allows concentration from large volumes on the column prior to desorption in a tight band. Together with selective elution in mixed hydrochloric and perchloric acids, this provides for the rapid and selective trace determination of a number of heavy metal ions.

## Discussion

Curiosity regarding the minima in several distribution ratio curves (Figure 18) led to a series of additional experiments with mercury(II), reported in Table IV. Several things can be deduced from these data. First, mercury(II) does not partition appreciably in perchloric acid alone, suggesting that chloride is present in the extracted complex(es). Second, increasing hydrogen ion concentration at constant ionic strength impedes the extraction, suggesting formation of undissociated chloroacids (40). Third, as perchlorate decreases, holding pH and chloride ion concentration constant, the distribution ratio increases. This indicates that perchlorate is not present in the partitioning species and/or that this is at least in part an anion exchange phenomenon rather than sorption of a neutral complex. Examination of the distribution data for mercury(II) in Table III shows a decline in adsorption from 10$\underline{M}$ HCl-5$\underline{M}$ $HClO_4$ to a minimum at 1$\underline{M}$ HCl-4.5$\underline{M}$ $HClO_4$. This is followed by a sharp rise in distribution ratio at gradient compositions lower in chloride content. Calculations based on the successive formation constants of mercury(II) chlorocomplexes indicate this minimum coincides with a sharp drop in the relative abundance of $HgCl_4^{2-}$, predominant at higher chloride concentrations, and a corresponding increase in the proportions of both $HgCl_3^-$ and $HgCl_2$ (41). Data reported for anion exchange adsorption of mercury(II) from hydrochloric acid alone

Table IV. Anion Exchange Weight Distribution Ratios for Mercury(II)

| $[H^+]$ | $[ClO_4^-]$ | $[Na^+]$ | $[Cl^-]$ | Dw |
|---|---|---|---|---|
| pH 1 | 0.9M | 0.9M | 0.1M | 22.4 |
| pH 1 | 4.9M | 4.9M | 0.1M | 14.5 |
| 1M | 1M | -- | -- | <0.5 |
| 5M | 5M | -- | -- | <0.5 |
| 5M | 4.9M | -- | 0.1M | 9.75 |

also indicate a maximum at very low acid concentrations with the distribution ratio diminishing as acid concentration increases.

This evidence seems to indicate preferential uptake of $HgCl_3^-$ and possibly $HgCl_2$ by the perchlorate form of the exchanger, at low chloride concentrations. As chloride concentration increases $HgCl_4^{2-}$ and $HHgCl_4^-$ are formed in the aqueous phase but compete poorly with perchlorate for the exchange sites, thus the adsorption minimum. Finally, at very high concentrations of chloride, where a large fraction of the resin is in the chloride form, these tetrachloro species are strongly taken up.

The distribution ratios of ruthenium(IV) and chromium(VI) in Table III were much less than expected based on previous data (5,42). Because ruthenium(III) and chromium(III) should be less strongly sorbed, spectral studies were conducted to confirm the oxidation states of the metals studied. Trace amounts of chromic acid were dissolved in 5$\underline{M}$ HCl-2.5$\underline{M}$ $HClO_4$ and in 5$\underline{M}$ $HClO_4$ and spectra run immediately. In both cases the spectra indicate formation of a mixture of $HCrO_4^-$ and $H_2CrO_4$. On standing for 10 hr the spectrum in perchloric acid remains unchanged whereas in the acid mixture almost complete conversion to chromium(III) has occurred with only minor amounts of chromium(VI) remaining, presumably containing $CrO_3Cl^-$ (43).

The spectrum of ruthenium(IV) was run after diluting the stock solution in 10M HCl. The spectrum obtained was the same as obtained by Wehner and Hindman, indicating that the solution contains a mixture of $Ru(OH)_2Cl_4^{2-}$ and at least one other complex of tetravalent ruthenium. The presence of trivalent ruthenium is therefore doubtful especially due to the ability of this ion to reduce perchlorate or dissolved oxygen (44). Bearing in mind the procedure employed in preparation of these ions, there can be no ambiguity about oxidation state. Partial oxidation of the resin, forming chromium(III), must be also ruled out because of the large molar absorptivity of the eluted peak and absence of separated peaks for chromium(III) and chromium(VI) in 10M HCl. It must be concluded that at least one detectable complex of these two ions is poorly sorbed to this resin.

# CONCLUSION

It is clear from the data presented that forced-flow anion exchange chromatography is a useful tool in the rapid and selective analysis of a variety of heavy metals in hydrochloric acid. Separation time has been reduced to five minutes per element or less. Continuous spectrophotometric monitoring of column effluents enables simultaneous quantitation of separated ions. This results in at least a 20-fold decrease in analysis time. Exceptional selectivity is obtained for some ions. To interfere an ion must be adsorbed and desorbed in the same eluent concentrations as the metal to be determined. Also, it must absorb at the same detection wavelength. Careful selection of elution conditions and detection wavelength can eliminate most interferences. With careful control of flow rate and elution time, reproducibility rivals or surpasses that obtained in most instrumental methods for the analysis of small amounts of metal in complex matrices. Calibration plots for the same column are valid indefinitely. Reproducibility of peak height from a single weighing greatly surpasses that between weighings. Because error is random, accuracy is limited by sample preparation and not by instrumental instability. Yet, accuracy on triplicate weighings of NBS standard samples is better than ± 2%. Because of the ability to concentrate from large sample volumes before elution, sensitivity is a function of sample volume. Quantitative determination of many metals is possible at the microgram level (peak height greater than 0.01 absorbance unit). Detection limits in the sub-nanogram range should be possible with proper attenuation. Finally, the cost of construction and operation is small even when compared with noninstrumental methods of analysis. Construction of a similar chromatograph that incorporates programmable wavelength and signal attenuation is estimated at $4,500. Helium expenditure is small with one tank (2800 $ft^3$) often lasting a month with continuous operation.

This technique has been demonstrated to be applicable to a range of sample sizes and matrix compositions. Along with the value of this technique in analysis for single elements, the ability to analyze exhaustively a mixture of metals has been demonstrated. Applications to trace metal analysis in water, body fluids, and foods seem promising. The complete analysis of brass and similar alloys is also possible.

## FUTURE WORK

Although forced-flow liquid chromatography has been demonstrated to be useful in separation and detection of metals by anion exchange in hydrochloric acid, the utility of this technique is not limited to this system. The ability to act as both eluent and spectrophotometric reagent is not peculiar to hydrochloric acid. The use of eluents containing thiocyanate, cyanide, bromide, or iodide should also provide many rapid and selective methods for metal ions on both anion and cation exchange resins. Nor is this technique limited to eluents that form light absorbing complexes; Sickafoose has demonstrated that a number of metals can be determined by mixing a color forming reagent and buffer with the column effluent (45). The use of ion exchange is not even necessary. More recent work by Goodkin has shown that heavy metals can be separated and determined on a resin with no ionic sites using this technique (46). It is clear, therefore, that this technique has great potential much of which is yet to be realized. Continued research in column chemistry, including development of new resins and more versatile elution media, is justified.

Of immediate interest in advancement of this technique is development of a high pressure eluent delivery system. This system must be corrosion resistant and capable of programmed eluent composition. Such a system would enable reproducible and unattended separation of a large number of metal ions.

For example, a delivery system capable of programmed mixing of either 5M perchloric acid or water with 10M hydrochloric acid would allow concentration and separation of up to 30 different elements on a single column of anion exchange resin. This development should be accompanied by detector modification to include addition of a photomultiplier and attenuator. This should increase sensitivity 100 fold and allow determination of some metals at the nanogram level. Such modification will also allow determination of metal mixtures with widely varying individual peak heights.

Finally, there exists a need for development of new detectors. Although UV-visible spectrophotometric detection has proven adequate for many applications, detectors are needed with even greater sensitivity, stability and/or selectivity. Great advances in inorganic analysis will arise from interfacing forced-flow chromatography with various instrumental methods of analysis. Even with methods that display selectivity in themselves, there is much to be gained from pre-analysis chromatographic sample processing. The sample can be first concentrated from a large sample volume followed by sequential elution by simply altering eluent composition. The identity of the element can be obtained from its retention time; its quantity can be determined from the height of the recorded peak. Problems with matrix interferences are eliminated. This can only add to the sensitivity, selectivity and reproducibility of methods like atomic emission spectroscopy, scintillation spectrometry and exhaustive coulometry.

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# ACKNOWLEDGEMENTS

The author wishes to thank James S. Fritz for his interest in, and critical evaluation of, the research herein described. The help of John P. Sickafoose, I. Louise Goodkin, Dean D. Woods, and James F. Jensen in design, construction, and refinement of the chromatograph is gratefully acknowledged.