# MICROANALYSIS OF METALS THROUGH THE USE OF CHELATING POLYMERS

A Dissertation Presented to the Faculty of the Department of Chemistry College of Arts and Sciences University of Houston

In Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy

by

Wilhelm Bruening August, 1970

# 545247

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#### ABSTRACT

The analytical properties of the chelating polymers poly-glyoxal bis-2-hydroxyanil (poly-GBHA) and poly-glyoxal bis-2-mercaptoanil (poly-GBMA) and their applications were investigated. Both chelating polymers were coated on an inactive support (Chromosorb W) and then used in a column "filtration" procedure. Poly-glyoxal bis-2-mercaptoanil is suitable for selective enrichment of gold from natural water samples, especially those with relatively high salt content. The effect of colloidal gold, salt concentration, flow rate, interferences, and the elution from the column were studied in detail.

The chelation and elution properties of poly-glyoxal bis-2-hydroxyanil were investigated for the microanalysis of copper, nickel, and cobalt. The effects of pH, metal concentration (copper, nickel, cobalt), flow rate, and interferences were extensively studied. The technique was applied to the analysis of the three metals in distilled and sea water.

ii

# TABLE OF CONTENTS

CHAPT	ER		PAGE
	АСК	NOWLEDGMENT	i
	ABS	TRACT	ii
Ī.	INT	RODUCTION	1
II.	GEN	IERAL REMARKS	3
	Α.	Bonding, Structure, and Selectivity of poly-GBHA and poly-GBMA	3
	Β.	Synthesis of Chelating Polymers	10
	C.	Application of Chelating Polymers	12
		1. Trace Concentration and Separation	12
		2. Analysis of Metal Complexes	13
		3. Chromatographic Separations	13
		4. Nuclear Chemistry	13
III.	THE IN	APPLICATION OF POLY-GBMA TO THE MICROANALYSIS OF GOLD	14
	Α.	Introduction	14
	Β.	Experimental	15
	•	1. Sample Preparation	15
		2. Preparation of Column Packing Material	15
		3. Preparation of Column	15
		4. Concentration Procedure	15
		5. Apparatus	16
		6. Chemicals	. 17

HAPTE	ER			PAGE
	C.	Resu	ults and Discussion	17
		1.	Standard Curves	17
			a. Experiments with Ionic Gold Solutions	17
			b. Experiments with Colloidal Gold Solutions	19
			c. Effect of MIBK-Solubility	22
		2.	Column Properties	24
			a. Effect of Salt Concentration on Chelation	24
			b. Effect of HCl Concentration on Chelation	24
			c. Column Regeneration and Elution	27
			d. Effect of Flow Rate	34
			e. Applications	34
			f. Interferences	36
IV.	THE COPI	APPL PER.	LICATION OF POLY-GBHA TO THE MICROANALYSIS OF	38
	Α.	Inti	roduction	38
	Β.	Expe	erimental	38
		1.	Preparation of Columns	38
		2.	Apparatus	39
		3.	Chemicals	39
		4.	Recommended Concentration Procedure	39
	c.	Resi	ults and Discussion	41
	- •.	1.	Range of Quantitative Chelation and Capacity of the Column	41

٠.

,

	2.	Effects on Chelation and Elution 43
		a. Chelation
		(1) Copper Chelation Curves 44
		(2) Nickel Chelation Curves
		(3) Cobalt Chelation Curves 47
		b. Elution
		(1) Copper Elution Curves 49
		(2) Nickel Elution Curves 49
		(3) Cobalt Elution Curves
		c. Conclusions Regarding Chelation and Elution 52
	3.	Standard Curves
	4.	Applications
		a. Distilled Water 61
		b. Sea Water 61
	5.	Interferences
		a. Cation Interferences during Copper Chelation 64
		b. Cation Interferences during Nickel Chelation 64
		c. Interferences during Cobalt Chelation 64
۷.	CONCLUS	IONS
	BIBLIOG	RAPHY

# LIST OF TABLES

TABLE		PAGE
I.	Effect of Temperature of MIBK-Solubility	23
II.	Effect of Salt Concentration on MIBK-Solubility	23
III.	Effect of HCl Concentration on MIBK-Solubility	23
IV.	Effect of Salt Concentration on Chelation	25
۷.	Effect of HCl Concentration on Ionic Gold Solutions $\ldots$ .	26
VI.	$H^+$ Concentration for Maximum Chelation	28
VII.	Effect of HCN Concentration on Quantitative Elution $\ldots$	30
VIII.	Effect of Hydrogen Ion Concentration on Gold Elution with Thiourea	30
IX.	Elution from the Column	33
Χ.	Effect of Flow Rate on Percent Chelation	35
XI.	Analyses of Gold Solutions in the Presence of Large Amounts of Base Metals	37
XII.	Instrumental Parameters Used for the Analyses of Copper, Nickel, and Cobalt	40
XIII.	Working Range and Capacity	40
XIV.	Parameters of the Standard Curves	57
XV.	Effect of Sea Water Concentration on Quantitative Recovery of Copper, Nickel, and Cobalt	63
XVI.	Influence of Interfering Metals on Copper Chelation	65
XVII.	Influence of Interfering Metals on Nickel Chelation	65
XVIII.	Influence of Interfering Metals on Cobalt Chelation	66
XIX.	Influence of Some Anions on Cobalt Chelation	68

# LIST OF FIGURES

FIGU	RE		PAGE
1.	GBHA and GBMA	•	3
2.	GBHA and GBMA Metal Complex Forms	•	4
3.	Stuart-Briegleb Model of the Ni-(II)-GBHA Complex	•	5
4.	Zwitterionic Structure of the GBHA Metal Complexes	•	6
5.	Stuart-Briegleb Model of the Gold-(III)-GBMA Complex	•	7
6.	Heterocyclic Five Membered Ring of the GBHA Metal Complexes	•	7
7.	Metal complex Structure of Malonaldehyde Bis-2- Hydroxyanil	•	8
8.	Structures of poly-GBHA and GBMA Metal Complexes	•	10
9.	Standard Curve Obtained from Ionic Gold Solutions	•	18
10.	Standard Curve Obtained from Colloidal Gold Solutions	•	20
11.	Standard Curve from Oxidized Colloidal Gold Solutions	•	21
12.	Redox Reaction Between poly-GBMA and Au-(III)	•	32
13.	Range of Quantitative Chelation and Capacity of the Column $% \mathcal{L}_{\mathcal{A}}$ .	•	42
14.	Effect of pH on Copper Chelation	•	45
15.	Effect of pH on Nickel Chelation	•	46
16.	Effect of pH on Cobalt Chelation	•	48
17.	Effect of pH on Copper Elution	•	50
18.	Effect of pH on Nickel Elution	•	51
19.	Effect of pH on Cobalt Elution	•	53
20.	Chelation of Copper, Nickel, and Cobalt at a Concentration of lo ppb and 2 ml/min Flow Rate	•	54
21.	Elution of Copper, Nickel, and Cobalt at a Concentration of 10 ppb and 2 ml/min Flow Rate	•	55

# LIST OF FIGURES (CONTINUED)

FIGU	RE																								PAGE
22.	Copper	Standard	Curve	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	58
23.	Nickel	Standard	Curve	•	•	•	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	•	•	•	•	59
24.	Cobalt	Standard	Curve	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	60

# I. INTRODUCTION

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#### I. INTRODUCTION

In analytical chemistry chromatographic methods have become indispensable for the separation of chemically similar substances, especially if one or more of these are present in trace amounts. In the field of inorganic analysis, ion exchange resins are often employed for the chromatographic separation of cation mixtures. During the last decade this area has been extended by the development of high molecular weight, cross-linked chelating exchange resins.

Although these resins are frequently called ion exchange resins, they are distinguishable from the conventional type of ion exchanger by three main properties (1):

a. High selectivity

The affinity of particular metal ions to a certain chelating ion exchanger depends mainly on the chelating group and not on the size of the ion, its charge, or other physical properties which determine the order of preference in the case of the ordinary ion exchanger.

b. Bond strength

In conventional ion exchangers, the binding is electrostatic with a strength of the order of 2-3 kcal/mole, while in the resins dealt with here the binding energy is of the order of 15-25 kcal/mole.

c. <u>Kinetics</u>

In the ordinary type of exchanger, exchange processes are more rapid and controlled by diffusion only, which is itself a function of the mobility and the concentration gradient of the ions entering and leaving. The exchange process in chelating exchangers is, however, slower and controlled either by a particle diffusion mechanism or by a second order chemical reaction.

In order to indicate these differences, the expressions "chelating polymer" instead of "ion exchange resin" and "chelation" instead of "ion exchange" will be used.

The most conspicious feature of chelating polymers is their ability to chelate selectively metal ions. This selectivity is based on the differences in stability of the complexes formed between metal ion and chelating polymer which can be varied to a large extent by changing the analytical conditions such as pH value, temperature, and addition of complex forming compounds. The accomplishment of the last possibility would contribute to the solution of some difficult analytical problems, such as the separation of similar ions and the enrichment of trace elements, in a simpler and far less tedious manner than by methods applied so far. During the past decade this challenge has encouraged numerous attempts at synthesizing chelating polymers that show a definite selectivity toward certain ion or groups of ions (2-9). Without doubt, in analytical as well as in preparative inorganic chemistry, there exists a need for chelating polymers.

Bayer and his co-workers at the University of Tubingen/Germany were able to synthesize two selective chelating polymers--poly-(glyoxal bis-2-hydroxyanil) (GBHA) and poly-(glyoxal bis-2-mercaptoanil) (GBMA) (10,11). The properties of both polymers in the microanalysis of metals is the subject of the present investigation.

# II. GENERAL REMARKS

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# **II. GENERAL REMARKS**

# A. Bonding, Structure and Selectivity of poly-GBHA and poly-GBMA

For the investigation of the structure and bonding of poly-GBHA and poly-GBMA, the monomeric low molecular-weight models were successfully used (12). GBHA and GBMA exist in two forms and their structure is shown in Figure 1.





Figure 1. GBHA and GBMA  $\gtrsim$ 

In weakly alkaline media, the ring forms (a) and (c), which are incapable of forming complexes, rearrange to yield the open chain forms (b) and (d), which are the true complexing agents. Because there is an equilibrium between the ring isomers and the open chain isomers even in acidic media, complex formation between metal ion and open chain isomer is possible, if the most strongly complexing ions  $Cu^{+2}$ ,  $UO_2^{+2}$ , Ni<sup>+2</sup>, and  $Co^{+2}$  in case of the GBHA and  $Au^{+3}$  in case of the GBMA are present. The rearrangement yields the complex forms shown in Figure 2.



 $M = Cu^{+2}; UO_2^{+2}; Ni^{+2}; CO^{+2}.$ 



Figure 2. GBHA and GBMA metal complex forms

GBHA also forms less stable complexes in weakly alkaline media. However, these complexes are not of interest here because the polymer is not stable at pH values larger than 7 and undergoes hydrolysis. On the other hand, if the hydrogen-ion concentration is high enough, the GBHA-metal complex redissociates completely. Unfortunately, this is not possible in case of the gold-GBMA complex. Both complexes have similar structures and the only difference of the gold complex is the substitution of the oxygen atoms by sulfur. Therefore, the sulfur-gold interaction appears to be responsible for the incapacity of redissociation of the Au-GBMA complex. Stuart-Briegleb models of the Ni(II)-GBHA complex and of the Au(III)-GBMA complex are useful in explaining this suggestion.

In Figure 3, the Ni(II)-GBHA complex shows that the distance between the phenolic oxygen and the metal ion (Ni<sup>+2</sup>) is too large in order to be



Figure 3. Stuart-Briegleb model of the Ni-(II)-GBHA complex.

able to form a covalent oxygen-metal bond, or a firm electrostatic bond. However, the position of the nitrogen atoms is very favorable for the

formation of a covalent metal nitrogen bonding. Therefore, the GBHAmetal chelates can be considered as zwitterions whose stability depends on the metal-nitrogen bonding. The structure obtained by Bayer and his co-workers (12) is shown in Figure 4.



Figure 4. Zwitterionic structure of the GBHA metal complexes

The structure in Figure 4 shows the bonding of two water molecules in the fifth and sixth coordination places of the nickel complex. The distribution of the charges explains their very strong bonding. Not only is the water oxygen bonded to the central ion, but there is also a contribution by the interaction between the water hydrogen atoms and the phenoxide groups. Therefore, water cannot be removed without decomposition of the complex.

The Stuart-Briegleb model of the Au-GBMA complex is shown in Figure 5. Here, the distances between the gold atom and the two sulfur atoms are considerably shorter than the corresponding distances in Figure 3. Consequently, sulfur-metal bonds are sterically possible. As







Figure 6. Heterocyclic five membered ring of the GBHA metal complexes

a result of this, the total strength of the Au-GBMA bonding increases to such an extent that the gold cannot be removed by acid without hydrolysis of the GBMA molecule. Complex formation is thus determined by the metal-nitrogen bond plus metal-sulfur bond.

On the other hand, the GBHA complex formation is determined exclusively by the formation of the metal-nitrogen bond. If we assume this bond to be covalent, then a heterocyclic five membered ring results which is shown in Figure 6.

According to Figure 3, this ring can have planar structure and cyclic conjugation seems to be possible. There are several indications which support this suggestion: GBHA-metal complexes show a deep color with a corresponding new absorption maximum between 550-580 nm. Furthermore, their C=N double bonds show considerable shifted IR absorption bands to shorter wavelengths, and they are stable against hydrogenation. If conjugation in the five membered hetrocyclic ring would not occur, then the corresponding metal complexes of malonaldehyde bis-2-hydroxyanil, which are shown in Figure 7 should exhibit the same properties. However,





all physical and chemical properties are the same as in the free complexing agent. These results have led to the hypothesis (12) that the heterocyclic five membered ring (Figure 6) actually represents a non-benzenoid, nonclassical aromatic system. The conclusions drawn for the monomeric forms can be applied to a large extent to the polymers. The structures of Ni(II)poly-GBHA and Au(III)-poly-GBMA are shown in Figure 8.

Bayer (12) was the first to stress the principle that if a ligand, which in aqueous solution forms complexes with many different metal ions, is bound to a polymeric matrix, greater selectivity results, because the ligands have to assume a certain geometric arrangement in the polymer. The application of this principle to the poly-GBHA metal complexes is in agreement with the experimental results obtained. The polymer shows higher selectivity because now the strength of the metal bonding depends, in addition to the nitrogen-metal bonding, on the geometric arrangement of the polymer. For the poly-GBMA complexes the sulfur-metal bonding presents an additional factor, which leads to a further increase in selectivity. Therefore, poly-GBMA forms fewer complexes with metal ions than poly-GBHA.

Although poly-GBMA is probably the most selective chelating polymer which has ever been synthesized; its lack of selectivity is still relatively large if compared to an ideal chelating polymer which would show selectivity for a single metal ion. So far, such ideal selectivity can only be found in some sea water living organisms (13).

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# B. Synthesis of Chelating Polymers

Conventional ion exchangers are practically insoluble, cross-linked polymers that contain either basic or acidic functional groups in high

concentration. These functional groups are tightly attached to the polymer matrix and are commonly introduced into the basic solid co-polymer by a substitution reaction. Practice, however, has shown this method to be seldom applicable in the synthesis of chelating polymers (14).

The formation of a chelate polymer should yield a very selective polymer with sufficient mechanical and chemical stability, especially toward acids and bases, which are used for the regeneration of the polymer. The selectivity depends first on the type of functional groups and second on the structure of the matrix. Marshall and Nickless concluded the following essentials for the synthesis of a highly selective chelating polymer designed for a given separation (15):

a. A careful choice of the structure of the ligand polymer, not only of the chelating group involved, but also of the molecular structure surrounding this group.

b. A precise determination of the relative formation constants of the corresponding chelates which must be different by more than one order of magnitude.

c. A maximum compatibility between the polymer and the medium obtained either by adjusting the polymer structure or by using mixed-solvent media.

Poly-GBHA and poly-GBMA meet the requirements for selectivity, mechanical, and chemical stability. The formation of the functional groups and the solid matrix occurs simultaneously by the polycondensation of triaminophenol and diaminothiophenol, respectively, with a several-fold excess of glyoxal in a weakly alkaline solution (10,11,16). The structures of their nickel and gold complexes are shown in Figure 8.

## C. Application of Chelating Polymers

Although many different chelating polymers have been synthesized, analytical applications for only a few have been described. Their main fields of application include the following:

#### 1. Trace concentration and separation

This is the most important field of application of chelating polymers and offers new possibilities in quantitative trace separation and concentration. Although chelating polymers have already been used for different metal separations, one should understand this only as a first encouraging step forward into a new area of analytical chemistry, which is so promising that it is impossible to make any predictions concerning its possibilities.

A major contribution in this area was made by Hering (17,18). He concentrated quantitatively several transition and alkaline earth metals on chelating polymers containing amino-carboxylic groups. Then, the metals were eluted with dilute acids and the relationship between elution curves and pH was shown. From this, a new concept was defined, the decomplexation pH (DpH) during the metal elution, each metal will appear in the eluent with a certain characteristic pH. Correlation of the metal ion concentration leaving the column, versus the pH produces the desired DpH values, which may also serve to calculate the stability constants of the metals with the chelating polymers.

Turse and Rieman (19) and Pennington and Williams (20) absorbed quantitatively traces of copper from media of 1 M  $NH_4Cl$  and 0.5 M NaCl, respectively, on Dowex A-1, the only commerically available chelating polymer. Poly-GBMA was used to recover gold from natural waters with 25% salt content (21). These examples prove that the strong bond of the metals to the chelating polymer enables them to be extracted from very dilute solutions of high ionic strength. This accomplishment would not have been possible with conventional ion exchange resins.

# 2. Analysis of metal complexes

Soluble metal chelates can be separated on a column of a chelating polymer into the complexing agent and metal ion (22). This is a convenient method for the analysis of metal-complexes.

## 3. Chromatographic separations

On a chelating polymer loaded with a complex-forming ion, soluble chelating agents can be separated from each other by partial ligand exchange between chelating agents fixed on the polymer and those in solution. Hering (5) separated, in this way, amino acids on columns containing chelating polymers with amino-carboxylic groups. Latterell and Wlaton (23) separated in a similar way chemically similar amines. Lewandowski and Hering (5) prepared chromatographic papers containing a chelating polymer which provided very good analytical results. Berger, Meyniel and Petit (24) used a colloidal mixture of Dowex A-1 and cellulose and separated by thinlayer chromatography Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>, and Hg<sup>2+</sup>, Cd<sup>2+</sup>, Pd<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Bi<sup>3+</sup>.

### 4. Application in nuclear chemistry

The application of neutron activation to metal ions bonded to a chelating polymer results in a weakened metal ion-chelating polymer bond for those metal ions which undergo an n,  $\gamma$  reaction. By shaking the polymer with a solution containing the metal ion as carrier, the labelled ions can be released. In this manner a solution of high specific activity can be obtained (1).

# III. THE APPLICATION OF POLY-GBMA TO THE MICROANALYSIS OF GOLD IN NATURAL WATERS

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## III. THE APPLICATION OF POLY-GBMA TO THE MICROANALYSIS OF GOLD IN NATURAL WATERS

#### A. Introduction

The term "natural water" includes river, lake, and sea water. Relatively little work has been reported in the literature relating to the quantitative analyses of gold in river and lake water samples. The studies of Abbulaev, et al. (25) have involved the determination of gold in natural waters using neutron activation analysis. There are several publications concerning gold determinations in sea water using different analytical techniques (26-32). The purpose of this study was to find a quantitative method for the determination of gold which would be applicable to all types of naturally occurring waters. The various waters differ primarily in their salt content and it is precisely this which significantly influences the accuracy of the analytical procedure. Low concentrations of gold (parts per billion level) in natural waters are very difficult to analyze directly because of the sensitivity of existing instrumental methods as well as interferences by the presence of other elements. Under these circumstances the gold in the sample must first be concentrated. Some studies along these lines have been made by Chao (33) using an ion exchange resin column. The present investigation involves a concentration step which can be effected by chelation on a chromatographic column containing a support coated with poly-GBMA. The gold which is now present in chelate form lends itself to solvent extraction with methyl isobutyl ketone then to measurement by atomic absorption (34,35).

#### B. Experimental

## 1. Sample preparation

A 1000 ml sample is taken and its pH is adjusted to 7 if the sample is basic. This is followed by the addition of 10 ml of conc. HCl. Ten ml of a 1% aqueous bromine solution are then added and the sample is allowed to stand overnight.

## 2. Preparation of column packing material

To 10 grams of the chelate polymer, 1000 ml of pyridine are added and the mixture is refluxed for 10 minutes. The filtered solution is transferred to a 2000 ml beaker which contains 200 grams of Chromosorb W. The pyridine is then evaporated with stirring at room temperature. The dry Chromosorb W contains 2% of the chelate polymer.

This technique can be improved by the application of a Polytron (Brinkmann Instruments, Westbury, New York). It is used to obtain a colloidal suspension of the chelate polymer. Four grams of the polymer are suspended in one liter of ethyl alcohol. Two hundred grams of Chromosorb W are then added and the alcohol is removed by evaporation with stirring and drying at room temperature.

### 3. Preparation of column

Two and one-half grams of prepared packing material is transferred in the form of an aqueous suspension into a chromatographic column (30 cm x l cm) in such a way that the column filling contains no air bubbles. The packing is then washed with 500 ml of distilled water.

### 4. Concentration procedure

A 1000 ml sample is passed through the column at a flow rate of 2 ml/minute. The column is washed with distilled water until the quali-

tative chloride test with silver nitrate for the eluent is negative. The gold and organic phase are eluted from the column with 50 ml of concentrated hydrochloric acid into a 400 ml beaker. An additional 10 ml of hydrogen peroxide is passed through the column to remove any residual organic matter. Three-tenths gram potassium permanganate is added to disintegrate the chelate polymer. The solution is then evaporated to approximately 30 ml. Polymer residues are filtered off and the beaker and filter are rinsed with small portions of distilled water so that a final filtrate volume of 50 ml results. This volume is transferred into a 250 ml separatory funnel. Four milliliters of MIBK are added and the solution is shaken 5 minutes in the separatory funnel. After the separation of the two phases, the MIBK phase is transferred into a special centrifuge tube (125 mm x 7 mm; calibration volume = 4 ml). The separatory funnel is rinsed with small portions of MIBK and these are also transferred into the same centrifuge tube until the calibration mark is reached. The tube is sealed with a stopper and shaken several times to obtain a homogeneous solution. This step is followed by centrifugation for 3 minutes.

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5. Apparatus

A Perkin-Elmer Model 303 atomic absorption spectrophotometer equipped with a gold, hollow-cathode lamp and the conventional burner atomizer was used to obtain the experimental data. The following instrumental parameters were used: Range = UV, Wave length = 243 nm, Slit = 3 mm, Source = 14 ma.

## 6. Chemicals

A standard stock solution (0.3 mg/ml) of gold III is made by dissolving  $HAuCl_4 \cdot 3H_20$  in water (J. T. Baker Chemical Co., Phillipsburg, N. J., "Baker Analyzed" Reagent). The colloidal gold solution and the MIBK were obtained from Curtin Scientific Co., Houston, Texas. Chromosorb W (acid washed, 45/60 mesh) is available from Supelco Inc., Bellefonte, Penn. The chelate polymer was prepared by condensing 1,4-diamino-2,5dimercaptobenzene with glyoxal (11).

### C. Results and Discussion

Attempts to concentrate gold quantitatively by solvent extraction or ion exchange were unsuccessful, particularly when samples with salt concentrations above 1% were used. The main problem was to find a concentration method which would be independent of the amount of salt present. In order to simulate natural conditions, water from the Great Salt Lake containing less than 0.1 ppb gold was used and appropriately small amounts of gold standard solution were added.

The physical properties of poly-GBMA favor its coating on an inactive support (Chromosorb W), if it is used in a column chromatographic process. This improves the flow rate, increases the active surface area and diminishes swelling problems of the chelating polymer.

1. Standard curves

a. Experiments with ionic gold solutions

Figure 9 shows a standard curve obtained from ionic gold solutions under the following conditions: Figure 9. Standard curve obtained from ionic gold solutions.



Amount of column material	:	2.5	grams
HC1 concentration	:	0.1	Ň
Flow rate	:	2.0	ml/min

This curve covers a range from 0-10 ppb and the detection limit if 0.5 ppb. If the sample contains more than 10 ppb gold, the concentration range of the curve can be extended by appropriate dilution of the MIBK phase.

#### b. Experiments with colloidal gold solutions

Gold is present in natural water samples in both ionic and colloidal forms. It is, therefore, necessary to test the efficiency of chelation by the column for colloidal gold solutions. Figure 10 shows a standard curve established with colloidal gold solutions. The linearity of this curve is quite satisfactory, however, the sensitivity doubled in the case of ionic gold. This is because the column chelates ionic gold more efficiently than colloidal gold. The sensitivity can be improved by oxidizing the colloidal gold the  $Br_2$  (10 ml 1% aqueous solution) to ionic gold and then proceeding with the concentration procedure. Chao (36) has shown that this also has the advantage of preventing the adsorption of the gold by the walls of the container. Figure 11 shows the standard curve established with oxidized colloidal gold solutions. The sensitivity in this case is much better than that for unoxidized solutions and about the same as the ionic solutions.

The use of atomic absorption spectrometry, combined with the chelation procedures used here, permits the detection limit of this method to be 0.5 ppb per liter of sample. It is possible to lower the detection limit to considerably smaller values by passing the appropriate amount of sample through the column. Because the concentration procedure and measurement

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# Figure 10. Standard curve obtained from colloidal gold solutions



Figure 11. Standard curve from oxidized colloidal gold solutions

14


of the gold are completely independent from each other, techniques other than atomic absorption spectrometry could be applied as a means of measurement.

#### c. Effect of MIBK-solubility

In order to be able to obtain a relatively low detection limit, an MIBK to aqueous phase ratio of 1:12.5 was chosen during the extraction procedure. This ratio is equivalent to an MIBK volume of 4 ml only, and therefore, it was necessary to investigate the effect of some parameters influencing the solubility of MIBK in the acid-aqueous phase. In all extractions, the gold is quantitatively transferred into the MIBK-phase regardless of its volume. Consequently, the gold concentration measured by atomic absorption is directly proportional to the MIBK-solubility in the aqueous phase.

The influence of the following parameters was investigated:

Temperature Salt concentration HCl concentration

Table I shows the effect of temperature on the solubility of MIBK. Fifteen ml MIBK were added to 500 ml acid-aqueous phase with constant HCl-concentration. After three minutes of shaking and the separation of the two phases, the volume of the MIBK-phase was measured again at different temperatures.

In similar manner were the effects of salt and HCl-concentration investigated. The results are shown in the Tables II and III, respectively. The data obtained show that the influence of temperature, salt and HClconcentration is very large and requires compensation. The final MIBK

# TABLE I

EFFECT OF TEMPERATURE ON MIBK-SOLUBILITY

# Temperature MIBK-Volume 10°C 0.5 ml 25°C 3.3 ml 60°C 6.0 ml

# TABLE II

# EFFECT OF SALT CONCENTRATION ON MIBK-SOLUBILITY

Amount of Great Salt Lake-Water	MIBK-Volume
0%	3.3 m1
20%	6.2 m1
50%	8.5 m1

### TABLE III

### EFFECT OF HC1 CONCENTRATION ON MIBK-SOLUBILITY

Percent HC1	MIBK-Volume
7%	5.3 ml
14%	3.2 ml
21%	0.8 ml
28%	dissolution

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volume is, therefore, controlled by using specially calibrated centrifuge tubes (see Experimental, page 16).

#### 2. Column properties

#### a. Effect of salt concentration on chelation

The measurements shown in Table IV should indicate whether or not the column functions independently from the salt content during the concentration procedure. The samples measured contained different amounts of salt but constant amounts of ionic gold. The results show no dependence on the salt content when this chelating procedure is used prior to the measurement with atomic absorption. Its relative standard deviation was found to be 1.5%. It was still necessary to determine whether different salt concentrations have any influence on the oxidation procedure or on the atomic absorption results of the oxidized colloidal gold solutions. Table IV also shows the results obtained from samples in which the colloidal gold concentration was kept constant and the salt concentration was varied; its relative standard deviation was 2.2%. These results, like those for the ionic gold indicate that there is no significant influence by the salt concentration.

#### b. Effect of HCl concentration on chelation

This experiment was necessary because an acid solution is passed through the column and the gold is eluted from the column with concentrated hydrochloric acid. Thus, somewhere between these two concentrations there must be a point at which chelation and elution of the gold are in equilibrium. Table V shows the results obtained for ionic gold solutions in which the gold concentration was kept constant (10 ppb)

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# EFFECT OF SALT CONCENTRATION ON CHELATION

% Salt water from Great Salt Lake	Relative absorbance for 10 ppb ionic gold	Relative absorbance for 10 ppb oxidized colloidal gold
0	0.2798	0.2700
20	0.2749	0.2765
40	0.2692	0.2716
60	0.2700	0.2635
80	0.2765	0.2790
100	0.2782	0.2798

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TABLE V	
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H <sup>+</sup> concentration	Percent chelation by the column
pH = 10	52
pH = 7	88
pH = 5	100
0.1 N	100
0.5 N	100
1.0 N	- 100
1.5 N	. 100
2.0 N	100
3.0 N	90
4.0 N	71

EFFECT OF HC1 CONCENTRATION ON IONIC GOLD SOLUTIONS

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and the hydrochloric acid concentration was varied. According to these results, the ability of the column to chelate is independent of the HCl concentration, at least in the range between pH = 5 and 2 N. This is an advantage when compared with ion exchange procedures in which a pH not lower than 1.5 - 1.0 is generally required. Thus, where samples have a very high basic metal ion content, they may not be sufficiently acid to prevent these metals from precipitating. Quantitative chelation of a 1 liter, 10 ppb ionic gold sample by the column containing 2.5 grams column material is possible only at HCl concentrations between pH = 5 and 2 N.

In order to determine which HCl concentration provides maximum chelation, conditions were chosen under which the column could only chelate a part of the standard gold solution. The amount of column material was, therefore, reduced to 1.5 grams, the gold concentration raised to 300 ppb, and the maximum flow rate of 8 ml/min was used. The results shown in Table VI indicate a range of maximum chelation between pH 2 and pH 4. This range is in contrast to the standard condition which uses a 0.1 N HCl solution. This is to prevent adsorption by the sample container walls which is considerably higher at lower acid concentrations. It should be noted that the column can effectively maintain its chelation ability with 0.1 N HCl solutions. The column was able to chelate a 10 ppb gold solution quantitatively using a maximum flow rate of 8 ml/min.

c. Column regeneration and elution

Experiments to regenerate the column with hydrochloric acid turned out to be negative. This result has been discussed under II-A.

TABL	E١	/I
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рН .	Relative absorbance
8	0.0996
6	0.1475
4	0.4179
2 ·	0.4202
1	0.1593
0	0.0540

# H<sup>+</sup> CONCENTRATION FOR MAXIMUM CHELATION

Following the acid regeneration experiments, attempts were made to regenerate the column with a gold complexing reagent which is able to form stronger, soluble complexes with gold than poly-GBMA. The first complexing agent used was potassium cyanide, whose regeneration properties were investigated as follows:

One liter solutions containing 10 ppb of ionic gold were concentrated by chelation under standard conditions. These columns were then treated with 50 ml portions of different KCN concentrations to determine the range of quantitative elution. The results shown in Table VII indicate that quantitative gold elution could only be achieved with 1% KCN. Unfortunately, this solution is not applicable in practice because it destroys the function of the column almost completely by eluting also the poly-GBMA phase from the column. The elution is due to the relatively strong alkaline media of the KCN solution which causes hydrolysis of the chelating polymer. The effect of hydrolysis increases with the KCN concentration. It is still considerable at 0.1%, less at 0.01% and negligible at 0.001%. In an additional experiment, the pH of the 0.01% KCN solution was adjusted to 7, causing a decrease of its elution performance to 80%.

In order to avoid the difficulties experienced with KCN solutions, a complex reagent was required which should be able to form a stronger complex with gold than poly-GBMA in an acid aqueous media. Such a reagent is thiourea, and the experiments were carried out in the same way as before with KCN solutions; the difference being the need to find the hydrogen ion concentration at which maximum gold elution occurs. The parameters of thiourea concentration (0.1%), its volume and flow rate,

TABL	Ξ٧	II
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# EFFECT OF KCN CONCENTRATION ON QUANTITATIVE ELUTION

KCN concentration	Percent gold eluted
1.0%	100%
0.1%	94%
0.01%	91%
0.001%	80%

# TABLE VIII

# EFFECT OF HYDROGEN ION CONCENTRATION ON GOLD ELUTION WITH THIOUREA

Hydrogen ion concentration	Percent gold eluted
рН = 6	1
pH = 5	25
·pH = 4	46
рН = 3	63
pH = 2	76
pH = 1	86
0.2 N	93
0.3 N	92
0.4 N	90
0.5 N	85

and the gold concentration were kept constant and only the hydrogen-ion concentration was varied. The corresponding amounts of gold eluted from the column are shown in Table VIII. They indicate that maximum elution (93%) was obtained at an HCl concentration of 0.2 N. However, none of the experiments provided quantitative gold elution. Furthermore, the gold elution could not be improved by increasing the thiourea concentration, its volume, and decreasing its flow rate.

From this fact it was concluded that the gold should be bonded in two different ways to the column material. The bonding of the elutable gold was already shown and discussed in Figure 8 under II-A. This gold is eluted in its ionic form.

The gold not eluted is assumed to be elemental gold, resulting from the redox reaction shown in Figure 12.

Generally, aromatic mercapto groups undergo easily air-oxidation and form disulfide bridges. In fact, the synthesis of poly-GBMA is carried out under nitrogen atmosphere to avoid this reaction. This type of reaction and the reduceability of gold-(III) lead to the assumption that the redox reaction shown above really takes place and makes the column regeneration impossible. Therefore, the only way to obtain a complete gold elution is to destroy the poly-GBMA. This was achieved by addition of HCl followed by hydrogen peroxide. Through this procedure the destroyed polymer plus the gold are completely washed out of the column. In order to determine the HCl concentration which would provide quantitative elution, the following experiments were undertaken:



Figure 12. Redox reaction between poly-GBMA and Au-(III)

One liter solutions containing 10 ppb of ionic gold were concentrated by chelation on the columns under standard conditions. These columns were then treated with 50 ml portions of different HCl concentrations to determine the range of quantitative elution. The results, shown in Table IX, indicate that quantitative elution from the column is only possible with

# TABLE IX

# ELUTION FROM THE COLUMN

HC1 concentration	Percent gold eluted from the column
10 N	100
8 N	96
6 N	75
4 N	39
2 N	11

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with 10 N HC1. Even when 2 N HC1 is used, 11% of gold was eluted. This value should not be compared with the one in Table V where the 2 N HC1 solution still provided quantitative chelation. Here the elution from the column involves the use of 10 ml 30% hydrogen peroxide which has a considerable effect on the elution of the gold from the column.

d. Effect of flow rate

It has been shown that quantitative chelation for 10 ppb ionic gold solutions is possible with 2 N HCl and that the salt concentration is not a factor when a flow rate of 2 ml/min is used. The effect of flow rate with HCl, salt, and gold concentrations was evaluated. The optimum HCl concentration of 2 N and maximum quantities of gold (300 ppb, the column capacity for the calibration curves) and salt solution (Great Salt Lake water) were used in this evaluation. Table X shows that high flow rates do indeed affect the chelation process at extreme conditions. However, flow rates up to 3 ml/min still yield quantitative results and are quite suitable for these high ranges.

e. Application

The separation of gold from iron, copper, and nickel by cation exchange generally requires a pH of 1.0 - 1.5. At lower pH limits there is some compromise between improved recovery of gold anions and some loss leakage of base metals, for example, one may expect at a pH less than 1.0, some contamination of the eluent with traces of iron and nickel (37). By raising the HCl concentration from 0.1 N and 2 N, solutions containing iron, nickel, and copper in relatively high concentration (percent level) could be analyzed quantitatively in the presence of

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# EFFECT OF FLOW RATE ON PERCENT CHELATION

. Flow rate (ml/min)	10 ppb ionic gold in 2 N HCl	10 ppb ionic gold in 0.1 N HCl and brine solution	300 ppb ionic gold in 0.1 N HCl
]	100	100	100
3	100	100	100
5	91	7,8	79
8	78	55	65

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5 ppb ionic gold. The results are shown in Table XI. When one considers that the base metals were present in an excess of  $10^7$ , these results are quite good and the small deviations are almost negligible. This general procedure should be applicable to other solutions from electroplating, refining streams, and biological materials.

More than 100 samples of natural waters have been analyzed using the technique. These have included flooded mines, river in gold-bearing areas, hot springs, and salt lakes. The values ranged from less than 0.5 ppb to 20 ppb.

#### f. Interferences

Mercury interferes with chelation of gold by the column packing. This can be avoided by complexion of the mercury with  $NH_4I$ ((0.4 gr/liter of sample). Experiments have shown that the chelate is able to remove the gold without interferences from samples containing as high as 100 ppm of complexed mercury. Cyanide solutions also interfere with the chelation procedure, however, this interference can be obviated by first oxidizing the solution with potassium permanganatehydrochloric acid solution.

# TABLE XI

Sample	Relative absorbance
Pure standard 5 ppb gold solution	. 0.1013
2.0% Fe-(III) + 5 ppb Au	0.0947
2.5% Ni-(II) + 5 ppb Au	0.0996
4.0% Cu-(II) + 5 ppb Au	0.0980
1% Fe-(III) - 1% Ni-(II) + 1% Cu-(II) + 5 ppb Au	0.0964

# ANALYSES OF GOLD SOLUTIONS IN THE PRESENCE OF LARGE AMOUNTS OF BASE METALS

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# IV. THE APPLICATION OF POLY-GBHA TO THE MICROANALYSIS OF COPPER, NICKEL, AND COBALT

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#### IV. THE APPLICATION OF POLY-GBHA TO THE MICROANALYSIS OF COPPER, NICKEL, AND COBALT

#### A. Introduction

In the study of poly-GBMA the concern was to apply this chelating polymer to the specific problem of analyzing micro amounts of gold in natural waters, especially those with relatively high salt content.

In this part of the research, the object was different in that the analysis of a certain metal was only of secondary importance. The main aim was to provide basic information about poly-GBHA itself (metal chelation and elution properties) in order to make this chelating polymer accessible to various trace separation and trace concentration problems of copper, nickel, and cobalt. Although Bayer and his co-workers have published several papers (10,12,38-44) dealing with the synthesis and application of poly-GBHA, the properties of this chelating polymer for the analysis of metals have never been extensively investigated. Due to its suitability for copper, nickel, and cobalt analysis, atomic absorption spectrometry was used as a means of measuring their concentrations (45,46). Undoubtedly, other techniques could also be applied.

### B. Experimental

#### 1. Preparation of columns

The column packing material was prepared and packed in exactly the same manner as described under (III. Experimental 2 and 3) using a Polytron. The column washing was different because it was performed with 50 ml of 0.5 N hydrochloric acid and twice with 20 ml of distilled water to remove the hydrochloric acid.

#### 2. Apparatus

The same atomic absorption spectrophotometer as described under (III. B. 5) was used to obtain the experimental data. The instrumental parameters used for the analysis of copper, nickel, and cobalt are shown in Table XII.

#### 3. Chemicals

"Distilled water" containing less than 0.1 ppb of copper, nickel and cobalt was prepared by passing the available "distilled water" (containing 5.1 ppb Cu; 3.2 ppb Ni, and <0.1 ppb Co) first through the chelate containing column.

The standard stock solutions (0.1 mg/ml) were made by dissolving  $CuCl_2 \cdot 2H_2O$ ,  $NiCl_2 \cdot 6H_2O$ , and  $CoCl_2 \cdot 6H_2O$  (all of them were reagent cryst. grade) in water. The 0.1 percent ammonium pyrrolidine dithiocarbanate (APDC) solution was prepared by dissolving the corresponding amount of reagent in water.

APDC and methyl isobutyl ketone (MIBK) were obtained from Curtin Scientific Company, Houston, Texas. Chromosorb W (acid washed, 45/60 mesh) was available from Supelco Inc., Bellefonte, Penn.

#### 4. Recommended concentration procedure

The volume of the aqueous sample is chosen in such a way that the total amount of the metal to be determined is 1 to 10 micrograms. The hydrogen ion concentration of the copper samples is then adjusted to pH = 4.0, and for the nickel and cobalt samples to pH - 5.0, with dilute HCl and Fisher Buffer Solutions of the corresponding pH. Then, the sample is passed quantitatively through the chromatographic column using

# TABLE XII

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# INSTRUMENTAL PARAMETERS USED FOR THE ANALYSES OF COPPER, NICKEL, AND COBALT

Element	Wavelength	Slit	Source	Air Flow	Acetylene Flow
Copper	324.7 nm	1 mm	14 mA	19 liters/min	4 liters/min
Nickel	232.0 nm	0.3 mm	25 mA	19 liters/min	4 liters/min
Cobalt	240.7 nm	0.3 mm	30 mA	19 liters/min	4 liters/min

# TABLE XIII

# WORKING RANGE AND CAPACITY

Comment	Amount of copper chelated by the column				
(parts per billion)	Relative, (percent)	Absolute, (micrograms)			
100	100	100			
200	94	188			
300	66	198			
400	51	204			
500	41	205			

a flow rate of 5 to 10 ml per minute. The column is washed with distilled water until the qualitative chloride test with silver nitrate for the eluent is negative.

The elution and regeneration of the column are carried out with 50 ml of dilute hydrochloric acid using a maximum flow rate of 10 ml/min. The acid concentration for the three metals should be the following:

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Copper = 0.5 N
Nickel = 0.1 N
Cobalt = 0.1 N
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While the copper eluent can be directly, quantitatively transferred into a 250 ml separatory funnel, the pH values of the nickel and cobalt eluent have to be adjusted before to a pH of 2-4. This is followed by the addition of 1 ml 0.1 percent aqueous APDC solution and 10 ml of MIBK. The solution is then shaken for 3 minutes in the separatory funnel and the MIBK phase is transferred into a centrifuge tube, followed by centrifugation for 3 minutes and the measuring of the optical density by atomic absorption spectrometry. Finally, the value of the copper concentration of the sample is obtained from the standard curve.

### C. <u>Results and Discussion</u>

#### 1. Range of quantitative chelation and capacity of the column

In order to determine the range of quantitative chelation and the capacity of the column, 1000 ml of copper standard solutions with different copper concentrations and pH = 6 were passed with a flow rate of 2 ml/min through the columns. The results shown in Table XIII and Figure 13 indicate a quantitative chelation range at least from 0 to 100 ppb under these





conditions. Further, from the absolute copper chelation values, also shown in Table XIII, it can be assumed that about 200 micrograms of copper represent the maximum capacity of the column.

2. Effects on chelation and elution

The pH range of quantitative chelation and elution is a function of the copper concentration and the flow rate. In order to investigate these effects, both parameters were used in their extremes. In relation to the quantitative chelation range (0 to 100 ppb), 10 and 100 ppb of the three metals were chosen as the two extremes of concentration and 2 and 12 ml/min (maximum flow rate of the column) as the extremes of flow rate.

#### a. Chelation

One thousand ml standard solutions of the three metals (containing 10 and 100 ppb, respectively) were adjusted to suitable pH values of the chelation ranges using dilute hydrochloric acid and 10 ml buffer solution of the corresponding pH. The buffer solutions were added for the compensation of protons, which are released during the chelation process from the chelating polymer.

These solutions were passed through the columns at flow rates of 2 and 12 ml/min, respectively. The chelated copper was eluted with 50 ml 0.5 N hydrochloric acid and nickel and cobalt with 50 ml of 0.1 N hydrochloric acid. The difference in acid concentration was chosen to avoid larger volume changes of the eluent because its pH needs adjustment to 2-4 before the metals can be extracted with APDC into MIBK. This is not necessary in the case of the copper eluent. After the metals were extracted into MIBK, its concentrations were measured by atomic absorption spectrometry and the results were plotted versus pH.

(1) Copper chelation curves

The corresponding copper chelation curves are shown in Figure 14. Curves a and b correspond to 10 ppb copper concentration; curve a representing a flow rate of 2 ml/min. and b 12 ml/min. The curves c and d correspond to copper concentration of 100 ppb; curve c representing a flow rate of 2 ml/min and curve d 12 ml/min.

The curves show that the beginning of the chelation is only slightly affected by concentration and flow rate because the origin of all four curves lies within a relatively small range of pH. However, there is a larger effect of concentration on quantitative chelation (at 100%), as indicated by the shift of the curves to higher pH values at increased copper concentrations. The effect of flow rate on quantitative chelation is relatively small at 10 ppb, but larger at 100 ppb. This can be expected because the ability of the column to chelate copper is expected to be larger at 10 ppb than at 100 ppb, which is the limit of quantitative chelation as indicated above.

(2) Nickel chelation curves

The corresponding nickel chelation curves are shown in Figure 15. The curves show the same characteristic as the copper chelation curves. For all four curves, the origin is approximately the same, but quantitative chelation is largely affected by flow rates and concentrations. In comparison to the copper chelation curves, those of

# Figure 14. Effect of pH on copper chelation

- a) 10 ppb copper and 2 ml/min flow rate
- b) 10 ppb copper and 12 ml/min flow rate
- c) 100 ppb copper and 2 ml/min flow rate
- d) 100 ppb copper and 12 ml/min flow rate



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# Figure 15. Effect of pH on nickel chelation

- a) 10 ppb nickel and 2 ml/min flow rate
- b) 10 ppb nickel and 12 ml/min flow rate
- c) 100 ppb nickel and 2 ml/min flow rate
- d) 100 ppb nickel and 12 ml/min flow rate



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nickel are shifted about one pH unit to higher values. Furthermore, the nickel curves show a wider pH spread (from curve a to d) than those of copper.

The differences in chelation between copper and nickel can be explained by the differences in equilibrium constants. Copper forms a stronger complex with poly-GBHA than nickel. Consequently, its chelation curves are shifted to lower pH values and their spread is smaller.

(3) Cobalt chelation curves

The corresponding cobalt chelation curves are shown in Figure 16. The curves show the same characteristic as the copper and nickel chelation curves. Again, the origin of the curves if approximately the same, however, quantitative chelation is largely affected by flow rates and concentrations. In comparison to the copper and nickel chelation curves, those of cobalt are shifted to higher pH values. However, the shift between nickel and cobalt is relatively small. Therefore, their equilibrium constants should be of similar magnitude.

b. <u>Elution</u>

The columns were loaded by passing 1000 ml standard solutions of the three metals (containing 10 and 100 ppb, respectively) at pH = 6 and a flow rate of 2 ml/min through the columns to provide quantitative chelation. The metals were then eluted from the column using 50 ml acid solutions of different pH values, prepared from dilute hydrochloric acid and 3 ml of the corresponding buffer solutions, and flow rates of 2 and 12 ml/min, respectively. The copper, nickel, and cobalt concentrations

Figure 1	6.	Effect	of	pН	on	cobalt	chelatio	on
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- a) 10 ppb cobalt and 2 ml/min flow rate
- b) 10 ppb cobalt and 12 ml/min flow rate
- c) 100 ppb cobalt and 2 ml/min flow rate
- d) 100 ppb cobalt and 12 ml/min flow rate



of the eluate were measured by atomic absorption spectrometry and the values obtained were plotted versus pH.

(1) Copper elution curves

The corresponding copper elution curves are shown in Figure 17. Curves a and b correspond to 10 ppb copper concentration, curve a representing a flow rate of 2 ml/min and b of 12 ml/min. The curves c and d correspond to copper concentration of 100 ppb, curve c representing a flow rate of 2 ml/min and curve d of 12 ml/min.

The elution and chelation curves show the same characteristics. The beginning of the elution is only affected by the copper concentration and not by the flow rate. The completion of the elution is significantly affected by both concentration and flow rate. In contrast to the chelation there is now a shift to lower pH values. It should be noted that the copper elution in these experiments was performed with only 50 ml of acid solution. Therefore, by increasing this volume the elution range of curve b and d (high flow rate) could probably be reduced.

(2) Nickel elution curves

The nickel elution curves are shown in Figure 18. Their characteristics are the same as the corresponding chelation curves in Figure 15. Again, they show that the beginning of the elution is only affected by the concentration and not by the flow rate. However, the completion of the elution is largely affected by both parameters, and at 100 percent elution the spread to lower pH values (from curve a to d) is smaller in comparison to copper. This is due to the fact that the poly-

Figure 17. Effect of pH on copper elution

- a) 10 ppb copper and 2 ml/min flow rate
- b) 10 ppb copper and 12 ml/min flow rate
- c) 100 ppb copper and 2 ml/min flow rate
- d) 100 ppb copper and 12 ml/min flow rate

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#### Figure 18. Effect of pH on nickel elution

- a) 10 ppb nickel and 2 ml/min flow rate
- b) 10 ppb nickel and 12 ml/min flow rate
- c) 100 ppb nickel and 2 ml/min flow rate
- d) 100 ppb nickel and 12 ml/min flow rate



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GBHA-nickel complex is less stable than the corresponding copper chelate. For the same reason, the nickel elution starts at higher pH values.

(3) Cobalt elution curves

The cobalt elution curves are shown in Figure 19. Cobalt forms with poly-GBHA the weakest complex of the three metals, and therefore, its elution curves are located in a region of higher pH values than nickel and copper. However, the beginning and the completion of the elutions are influenced by the concentration and flow rate in the same way and tendency.

#### c. Conclusions regarding chelation and elution

An evaluation of the chelation and elution curves (Figure 14-19) indicates that the analytical qualifications of the column material for copper are better for the lower concentration range (0-10 ppb), because the pH range of quantitative chelation and the effect of flow rate is smallest here (only about 2 pH units).

Figure 20 and Figure 21 show, respectively, a correlation of chelation and elution between copper, nickel, and cobalt for this particular concentration range at a flow rate of 2 ml/min. The fact that chelation and elution occur at different pH values for the individual metals can be utilized for their separation. In Figure 20, at pH 3.76, 100% copper chelation is obtained, while nickel and cobalt are only chelated to 50% and 43%, respectively. The same pH would provide an elution of 57% cobalt, 50% nickel, and 0% copper, as shown in Figure 21. The results indicate that under the conditions used here, a 100% separation cannot be achieved. However, a complete separation between two of the three metals can probably

## Figure 19. Effect of pH on cobalt elution

- a) 10 ppb cobalt and 2 ml/min flow rate
- b) 10 ppb cobalt and 12 ml/min flow rate
- c) 100 ppb cobalt and 2 ml/min flow rate
- d) 100 ppb cobalt and 12 ml/min flow rate



Figure 20. Chelation of copper, nickel, and cobalt at a concentration of 10 ppb and 2 ml/min flow rate



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Figure 21. Elution of copper, nickel, and cobalt at a concentration of 10 ppb and 2 ml/min flow rate



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be obtained, if the liquid phase contains a complexing agent which is able to form a stronger soluble complex with one of the two metals than poly-GBHA.

These separating limitations of poly-GBHA do not largely effect its application in the trace analysis of these metals because the actual separation can easily be performed by instrumental methods (e.g., atomic absorption). However, in order to make these instrumental methods applicable, the samples very often need a preconcentration which can be achieved in a convenient manner by the chelating polymer. This is its main application feature.

The elution curves, shown in Figure 17-19, 21, provide information regarding the elution parameters. Quantitative elution can be performed for the lower concentration range (0-10 ppb) in any case with 50 ml of 0.1 N hydrochloric acid, even at a flow rate of 12 ml/min (Figure 17, curve b). On the other hand, the hydrolysis of the chelating polymer starts only a 1 N hydrochloric acid. Therefore, the use of stronger hydrochloric acid is recommended, if this is suitable for the metal determination, which is carried out later on.

3. Standard curves

Table XIV contains data of the parameters which were used to establish the standard curves for copper, nickel, and cobalt, shown in Figure 22-24, respectively.

The curves of nickel and cobalt show very good linearity, while the copper curve is slightly non linear at the beginning. The curves cover a range from 0-10 ppb and the detection limit is 0.5 ppb. If the sample

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## TABLE XIV

# PARAMETERS OF THE STANDARD CURVES

Element	Amount of column material	Standard solution volume	$H^+$ concentration	Flow rate
Copper	2.5 grams	1000 m1	pH = 4	4 ml/min
Nickel	2.5 grams	1000 m1	pH = 5	4 ml/min
Cobalt	2.5 grams	1000 m1	pH = 5	4 ml/min



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Figure 23. Nickel standard curve

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Figure 24. Cobalt standard curve

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contains more than 10 ppb copper, the concentration range of the curve can be extended by appropriate dilution of the MIBK phase, and the detection limit can be improved by using a MIBK to aqueous phase ratio of 1:12.5 in volume control.

#### 4. Applications

a. Distilled water

The "distilled water" in our laboratory was analyzed and the following results were obtained:

Copper = 5.1 ppb Nickel = 3.2 ppb Cobalt = <0.1 ppb

Consequently, all distilled water used for column washing and the preparation of standard solutions and reagents was first passed through the columns in order to cancel out the interferences of its copper and nickel content.

b. Sea water

Sea water contains numerous metals other than copper, nickel, and cobalt, and therefore, provides an excellent opportunity for a selectivity test. Sea water, taken at Galveston, Texas, was passed through the columns in order to lower the copper, nickel and cobalt content below the detection limit. The same water was then used again for the preparation of new 1000 ml samples containing different amounts of sea water but constant ionic amounts of the three individual metals. Their pH values were adjusted to 4 for copper and to 5 for nickel and cobalt; and then they were passed through the regenerated columns with a flow rate of 2 ml/min. Through this procedure it was possible to determine the following points of interest:

- a. Influence of sea water on quantitative chelation
- Quantitative recovery of the three metals from the original sea water sample

The results shown in Table XV indicate that the columns were indeed able to recover copper and nickel quantitatively from the original sea water and that its concentration does not effect their quantitative chelation. For nickel, however, the recovery could be completed only after the concentration of the chelating polymer on Chromosorb W was raised to 4%. The relative standard deviations for the determination of copper and nickel were 2.1% and 1.7%, respectively.

The final copper and nickel determination in sea water samples resulted in 6.4 ppb copper and 3.5 ppb nickel. On the other hand, the cobalt results show that the column is not able to function independently of the sea water concentration during the concentration procedure of cobalt.

5. Interferences

Cations, able to form chelates with poly-GBHA, interfere with each other during the chelation. Besides copper, nickel, and cobalt, the polymer is also able to chelate uranyl. Therefore, its interference was investigated in conjunction with those of the other three metals in the following way: 1000 ml samples were prepared containing 10 ppb of the metal to be determined and different amounts of one interfering cation. This cation was added in concentrations which increased always by one order of magnitude starting at 10 ppb.

### TABLE XV

	Re	lative absorb	ance
Percent sea water	Copper	Nickel	Cobalt
0	0.1475	0.1024	0.1314
20	0.1463	0.0996	0.0545
40	0.1555	0.0985	0.0259
60	0.1494	0.1007	0.0182
80	0.1494	0.1020	0.0123
100	0.1494	0.1007	0.0088

# EFFECT OF SEA WATER CONCENTRATION ON QUANTITATIVE RECOVERY OF COPPER, NICKEL, AND COBALT

#### a. Cation interferences during the copper chelation

The influence of the interfering cations during the copper chelation is shown in Table XVI. The interfering effect starts at a concentration of 10 ppm and decreases from uranyl to nickel to cobalt according to the strength of their poly-GBHA complexes.

#### b. Cation interferences during the nickel chelation

The influence of the interfering cations during the nickel chelation is shown in Table XVII. The analytical data were obtained with the same column material used for the nickel recovery from sea water (4% chelating polymer). In comparison to copper, the interferences begin at 1000 ppb and decrease in a manner similar to that of copper.

c. Interferences during the cobalt chelation

The influence of interfering cations during the cobalt chelation is shown in Table XVIII. The same column material (4% chelating polymer), as used for the corresponding nickel experiments, was employed in order to be able to make a proper comparison of the results. The interferences for cobalt start at the same order of magnitude as for nickel, but they are generally stronger which is in accord with the stabilities of the corresponding complexes.

On the other hand, a comparison between the uranyl interference (53% cobalt recovery) and nickel interference (20% cobalt recovery) does not agree with the previous results which indicate that nickel should interfere less than uranyl. The presumption that nickel would interfere during the atomic absorption part of the cobalt analysis was not confirmed experimentally. Since uranyl was only available as acetate and nickel was used as chloride,

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#### TABLE XVI

Concentration of	Percent copper recovered in the presence of		
the interfering metals	Uranium	Nickel	Cobalt
10 ppb	100	100	100
100 ppb	100	100	100
- 1000 ppb	100	100	100
10 ppm	81	89	96

#### INFLUENCE OF INTERFERING METALS ON COPPER CHELATION

#### TABLE XVII

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#### INFLUENCE OF INTERFERING METALS ON NICKEL CHELATION

	Percent copper recovered in the presence of		
the interfering metals	Copper	Uranium	Cobalt
10 ppb	100	100	100
100 ppb	100	. 100	100
1000 ppb	60	76	95

## TABLE XVIII

Concentration of	Percent cobalt recovered in the presence of		
the interfering metals	Copper	Uranium	Nickel
10 ppb	100	100	100
100 ppb	100	100	100
1000 ppb	18	53	20

#### INFLUENCE OF INTERFERING METALS ON COBALT CHELATION

the anions present during the two experiments were considerably different. In order to test the influence of acetate ions, the particular nickel experiment was repeated by adding an stoichiometric amount of acetate to the sample. Then the nickel interference decreased and cobalt was recovered to 55%. These results indicate an anion effect on chelation. This effect was studied more extensively by the following experiment: 1000 ml samples containing 10 ppb cobalt and 100 ppm of a certain anion were passed at pH 5 through the columns. The cobalt recovery values are shown (in percent) in Table XIX.

The results show considerable anion influence on cobalt chelation. Special attention should be paid to the remarkable interferences caused by cyanide and sulfate. The data in Table XIX are suitable to explain the negative results obtained in the cobalt recovery from sea water. It may be assumed that cobalt forms a number of relatively stable complexes with ligands present in sea water. These compete with the cobalt-poly-GBHA complex preventing in this way the quantitative chelation of the cobalt.

67

## TABLE XIX

#### INFLUENCE OF SOME ANIONS ON COBALT CHELATION

Anion	Percent cobalt chelated
C1 <sup>-</sup> .	100
I_	90
SCN	85
s04	60
CN	0

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### V. CONCLUSIONS

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In this work an attempt has been made to extend the general analytical knowledge of the chelating polymers poly-GBHA and poly-GBMA with respect to their properties in trace concentration, separation, and purification. This was performed by simple filtrations in chromatographic columns containing the chelating polymers coated on Chromosorb W. Because of high selectivity and affinity to gold-(III), poly-GBMA was able to chelate gold under extreme conditions (25% salt content, high hydrochloric acid concentration), solving a quite difficult problem in gold analysis. Poly-GBHA was applied to the microanalysis of copper, nickel, and coablt. The selectivity is lower than that of poly-GBMA, and therefore, it is not quite as useful as a means of separation. However, its analytical value as a means of trace concentration was demonstrated and exemplified by the quantitative recovery of copper and nickel from sea water.

A further study should include the determination of the equilibrium constants of the chelates in order to be able to describe their strength quantitatively. In addition, the usefulness of poly-GBHA for the microanalysis of uranyl should be investigated.

The application of these polymers in analytical chemistry is definitely of great advantage because of their easy and time saving operation and their selectivity. In particular, this includes the concentration and difficult separations of metal traces. However, the field of chelating polymers is rather young and it is developing slowly because of the lack of commercially available suitable polymers. The synthesis of various types of chelating polymers with new structural features and a wide range of properties should be encouraged for enhancing analytical techniques. BIBLIOGRAPHY

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