

State of Alaska
Department of Natural Resources
Division of Geological and Geophysical Surveys
College, Alaska

LABORATORY NOTES - 18

AN INVESTIGATION INTO THE USE OF MIBK
AND DIBK-ALIQUAT 336 WITH ATOMIC ABSORPTION SPECTROPHOTOMETRY
IN THE ANALYSIS OF GOLD

By

W. W. McClintock and Thomas C. Tribble

June 1973

TABLE OF CONTENTS

Abstract	1
Introduction	1
MIBK Investigation	1 - 3
DIBK Investigation	4 - 8
Conclusions and Recommendation	9 - 10
Bibliography	

TABS

TAB I	Solubility effects of MIBK on analyses.
TAB II	Standard analysis curves.
TAB III	Volume changes MIBK due solubility.
TAB IV	Solubility of MIBK as effected by concentration and sequence of washing.
TAB V	Gold concentrations in aqueous and organic phases after various washings.
TAB VI	Test of analysis against nearly matched standards.
TAB VII	Graphic display of effect of differing concentrations standard and unknown.

ABSTRACT

The use of organic extraction agents MIBK and DIBK-Aliquat 336 are investigated in the determination of gold by AA spectrophotometry. The problems of solvent solubility and elemental interferences are considered. It is concluded that the DIBK-AQ 336 method is a good, perhaps outstanding, technique for gold determination.

INTRODUCTION

In the mineral preparation research work at the University and in the regular assay work at the Alaska Geological Survey, the two standard methods of gold assaying are aqua regia digestion followed by extraction into methyl isobutyl ketone prior to analysis by atomic absorption, and the fire assay technique. The first method is somewhat simpler and more readily accomplished, and is capable of lower quantitative detection limits, while the latter is the accepted umpire analytical method and is considered more accurate, especially in high concentrations. The AA method also has advantages in the analysis of liquids such as cyanide solutions and amalgams.

In the MIBK-AA method two problems are evident: The solubility of the MIBK in the aqueous phase, and the effect of interferences, most notably iron. The accepted solution to the iron interference is to back extract from the organic phase with dilute HCL, which in turn aggravates the solubility loss of MIBK into water and changes the resultant gold concentration in the remaining MIBK.

This MIBK-AA method, with its washings, requires considerable laboratory manipulation. It may be of little consequence if the amount of gold present is not in the range of the standards simultaneously prepared. Importantly, it has been estimated that only about 7% of the determinations of the State free assay program fall in the measurable range resulting in a considerable wasted expense.

It is the purpose of this study to investigate the MIBK-AA procedure, and if it is considered too laborious or inaccurate to further explore another method using a less soluble ketone with a complexing agent (Diisobutyl Ketone with Aliquat 336) which has been reported for use in gold analysis. (1) (2)

I. PROCEDURE

A. MIBK-AA Investigation

1. Preliminary discussion. In addition to the problems discussed in the introduction, that of the solubility of the MIBK in the aqueous phase resulting in a concentration of gold, and the iron interference, it was also suspected that the MIBK dissolving might carry some gold with it decreasing the gold concentration. And while the accepted solution to these problems has been to run the standards at the same time and under the same conditions as the unknowns, the exact conditions could not be duplicated because the composition of the material to be analyzed is unknown. Failure to match the standard and the unknown could effect the extraction efficiency and the solubility of the MIBK due to the common ion effect and the Satchenow salt effect (3).

2. Experimental procedure.

- a. It was decided to accept the available aqua regia digestion results, that procedure being the easiest to perform, the most amenable to other analyses, and considered of sufficient accuracy for the purpose, reportedly in the range of 99.5%.
- b. The following preliminary experiments were conducted:
 1. A known amount of gold was digested in aqua regia diluted to 35 ml and extracted into 10 ml of MIBK and analyzed against standards prepared from MIBK extractions of equal volumes of aqueous and MIBK phases. The MIBK previously having been saturated with the aqueous solution in each case. The MIBK was washed three times with 10% V/V HCl.
 2. A known amount of gold was digested in aqua regia made up to 35 ml and extracted into 10 ml of MIBK and analyzed as before, except that after evaporating the original digestate to moistness, the aqua regia used in redissolving it up was first saturated with MIBK. The MIBK was washed twice in 10% HCl, also saturated with MIBK.
 3. See Tab 1 for the approximate results, the procedure being too rough to be diagnostic, but giving rise to the following hypothesis.
 - a. The uncorrected standard, the fourth column of Tab 1 was made a 1:1 volume ratio of aqueous and MIBK, whereas the pseudo unknown was extracted with a ratio of 3.5:1 aqueous to MIBK. Although the volume ratios were different, the resulting apparent gold concentrations were similar, indicating unknown compensating effects are occurring.
 - b. In the case of the aqueous solution which had previously been saturated with MIBK, it appears that this MIBK is carrying some of the gold with it, and although the concentrating effect of the loss of MIBK through solubility is removed, a loss of gold simultaneously occurs.
- c. No simple way to improve accuracy by calculation is apparent.
- d. Investigation into the effect of iron and solubility.
 1. Four samples of measured amounts of gold to give 1, 3, 7, and 10 ppm concentrations in the MIBK phase if entirely extracted were prepared in 50 ml of 33% AR. Three of these also contained 5,000 ppm iron in the aqueous phase, the fourth no iron.

And a fifth set of standards was made up by adding directly to MIBK (not saturated with an aqueous phase) appropriate portions of 100 ppm gold standard.

I

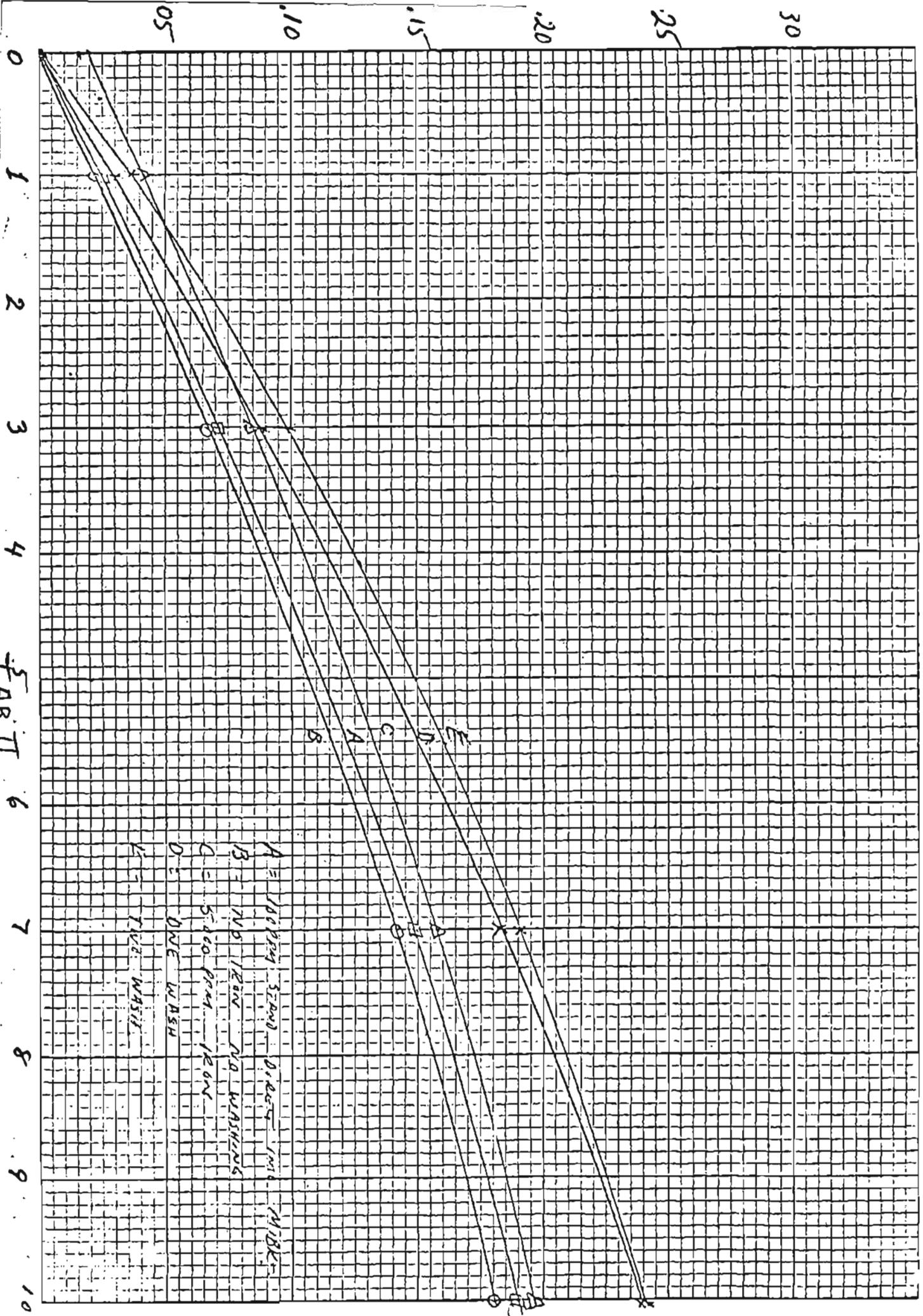
A. Aqueous phase not saturated with MIBK.

Sample or Process	Initial Dil (ml) Aq:Or = 35/10	Vol. After Extract	PPM Conc. Meas. Against Un-Corr. Stand	Corr'd Apparent Microgram (PPMXVOL)	Uncorr. Apparent Microgram (PPM X10)
No Wash	35/10	9.5	10.0	95.0	100
One Wash 10% HCl	35/9.5	8.8	10.8	95.0	108
Two Wash	35/8.8	8.1	11.8	95.0	118
Three Wash	35/8.1	7.4	12.8	95.0	128

B. Aqueous phase saturated with MIBK

No Wash	35/10	10	9.5	95	95
One Wash	35/10	10	9.3	93	93
Two Wash	35/10	10	9.1	91	91

TAB I



2. See the enclosed graph, Tab II for results. It is evident that the iron increases the apparent gold concentration and that it can be removed but the resulting concentrations are effected. No account is taken of the effect of the concentration of salts and gold on the apparent concentration of the gold or of the extractive efficiency. The difference between curve A and B, though not diagnostic, would indicate that not all the gold is extracted from the aqueous phase at least in this case.

e. Investigation into the effect of solubility.

1. Two extractions were made in a large separatory funnel, both extracting 500 micrograms of gold from 500 ml of 33% aqua regia into 100 ml of acid saturated MIBK. These extractions were washed three times, first with a 10% HCl solution, then twice with a 5% HCl solution. Aliquots of MIBK and of the aqueous solution were taken from each step, the MIBK, and MIBK extractions from the aqueous phases were analyzed in the same run and under the same conditions as the five curves in Tab II.
 2. Tabs III and IV show the effect of concentration of salts, in this case of HNO₃ and HCl on solubility. Test three was run under the same conditions as tests 1 & 2, without analyzing for gold, and the purpose of testing a variation of wash concentrations, being washed first with 5% HCl and subsequently with 10% washes.
 3. The graph in Tab V shows the actual concentration of gold in both the MIBK portion and the aqueous phase at each stage of the procedure. These were measured against the unwashed extraction curve, curve B of Tab II. The graph in Tab VI shows the gold measured against standard nearly matched in salt concentration and washing.
 4. From Tab III and IV it is apparent that the concentration of dissolved salts has a great effect both in the solution under consideration and in at least the first subsequent washing, some sort of supersaturation effect being hypothesized. While these could perhaps be worked out, it is enough to recognize that some system of matching salt in both the unknown and standard must be done, or some compensation arrived at. There is no consistent compensating correction readily apparent.
- f. Conclusion. The change in concentration of gold due to solution of part of the MIBK, as well as the loss of part of the gold in the dissolved MIBK, are both effected by numerous factors, especially salt concentration in the aqueous phase. This concentration cannot be matched between a standard and an unknown, thus it is desirable to find a method less effected, primarily through use of an extractant of lower solubility.

III

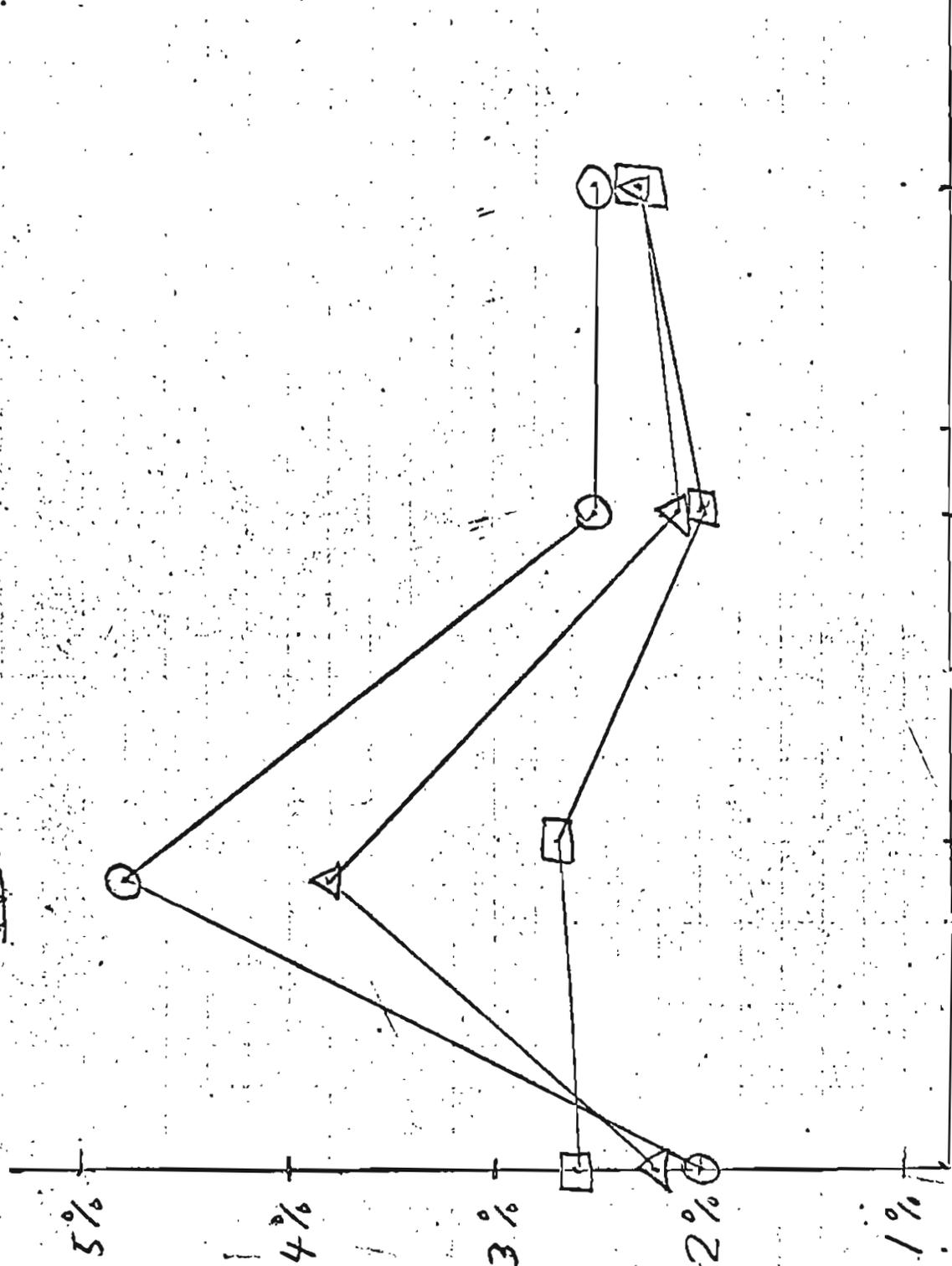
Solubility of MIBK given in volume, % of Aqueous phase, for various concentrations of wash solutions and sequence of washes. (The MIBK was first saturated in dilute aqua regia in all cases).

Wash Comp.	Test #1	Test #2
33% aqua regia	2.2	2.0
10% HCl	3.9	4.8
5% HCl	2.1	2.5
5% HCl	2.3	2.5
	Test #3	
33% Boiled aqua regia	2.6	
5% HCl	2.7	
5% HCl	2.0	
10% HC	2.3	

IV.

VOLUMETRIC PERCENT SOLUBILITY OF MIBIC (ACID SAT.) IN VARIOUS AQUEOUS PHASES IN DIFFERENT SEQUENCE.

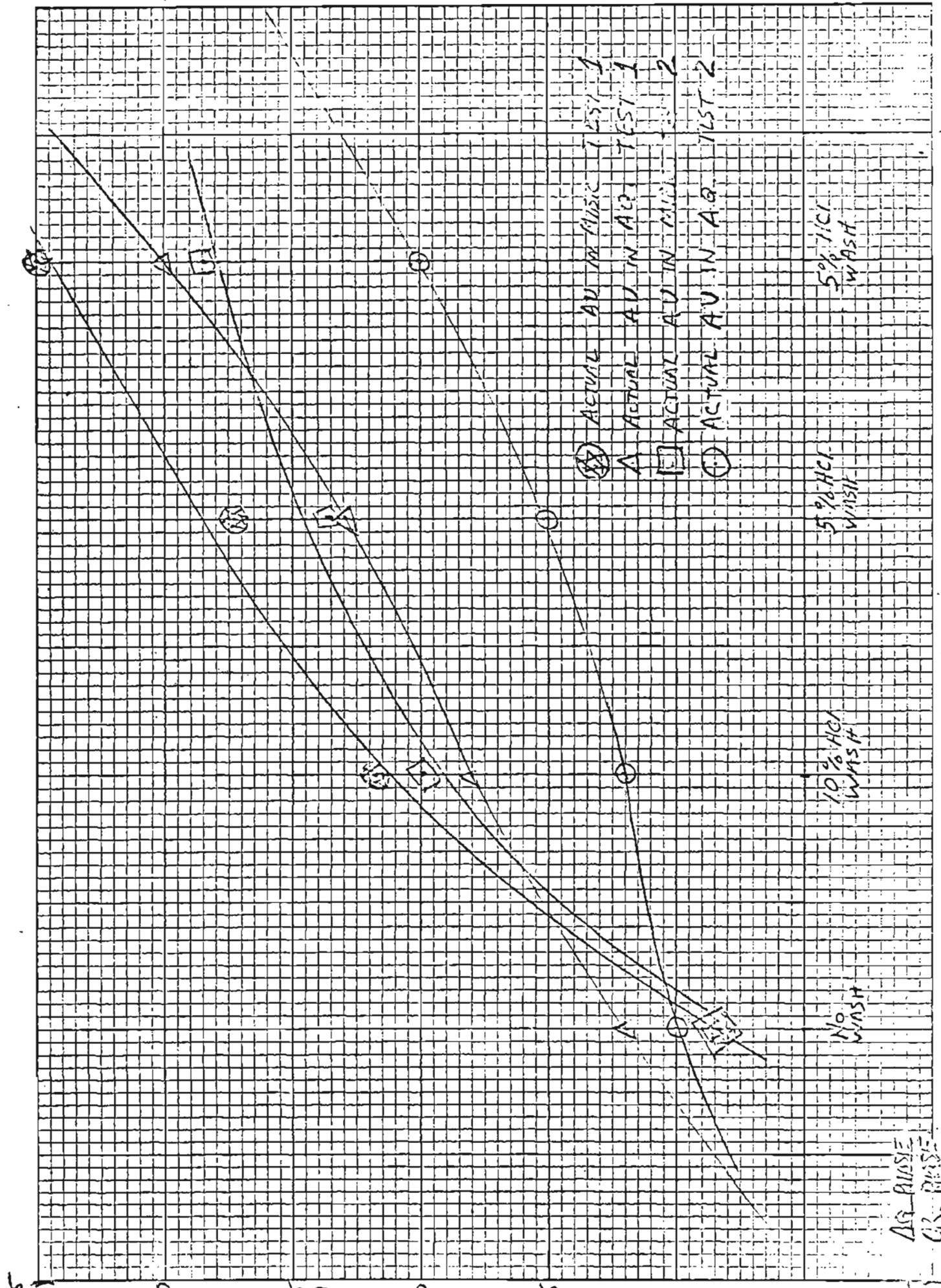
TEST 1 Δ
 TEST 2 \odot
 TEST 3 \square

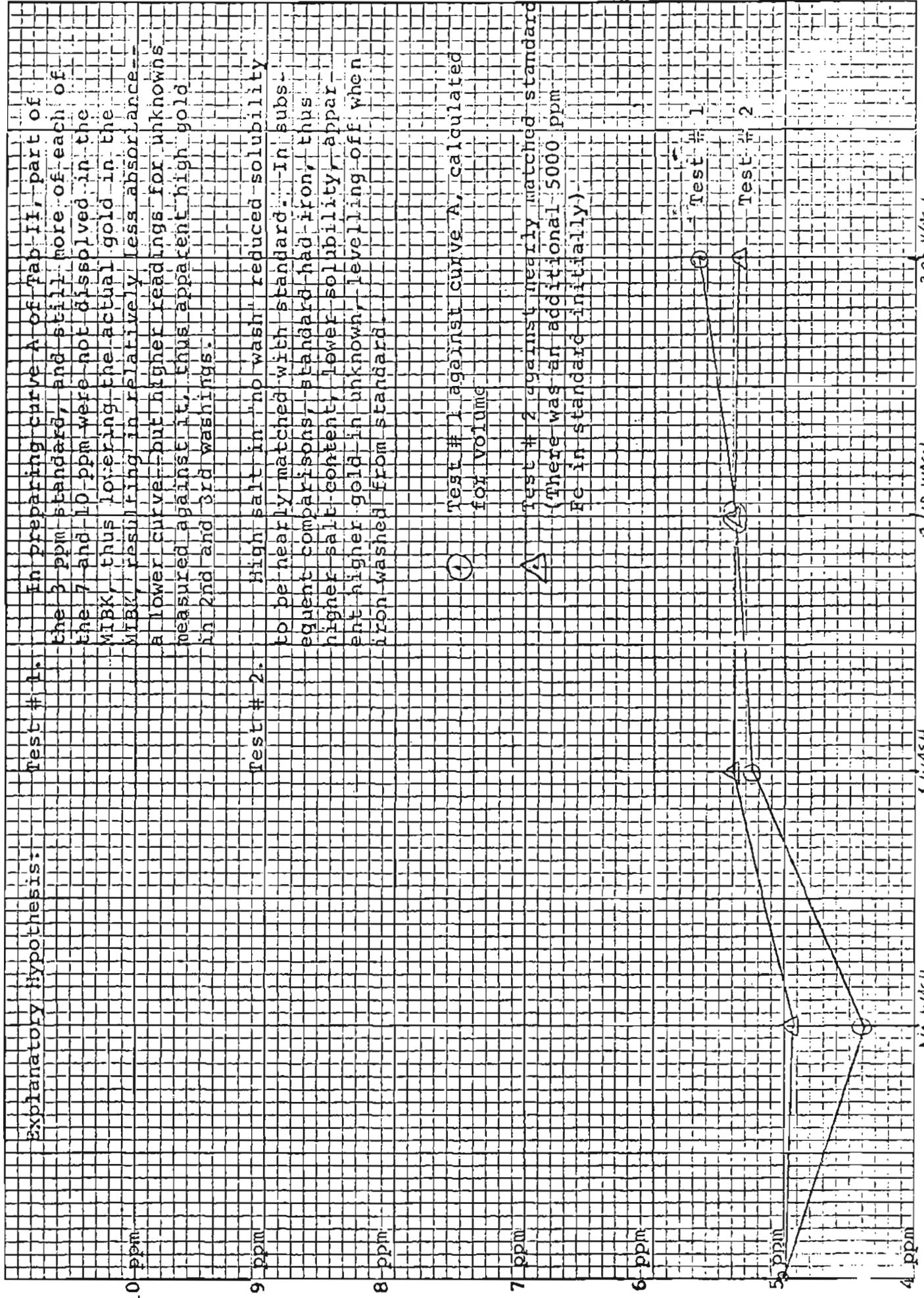


SEQUENCE 1
 TEST 1 + 2 33% AQUA REGIA 10% HCl 5% HCl 5% HCl 5% HCl.

SEQUENCE 2
 TEST 3 33% BOILED AQUA REGIA 5% HCl 5% HCl 10% HCl

TAB IV





Explanatory Hypothesis:

Test # 1.

In preparing curve A of Tab II, part of the 3 ppm standard, and still more of each of the 7 and 10 ppm were not dissolved in the MIBK, thus lowering the actual gold in the MIBK, resulting in relatively less absorbance-- a lower curve-- but higher readings for unknowns measured against it, thus apparent high gold in 2nd and 3rd washings.

Test # 2.

High salt in "no wash" reduced solubility to be nearly matched with standard. In subsequent comparisons, standard had iron, thus higher salt content, lower solubility, apparent higher gold in unknown, levelling off when iron washed from standard.

Test # 1 against curve A, calculated for volume

Test # 2 against nearly matched standards, (There was an additional 5000 ppm Fe in standard initially)

Test # 1

Test # 2

NO WASH
 1 WASH 10% HCl
 2ND WASH 5% HCl
 3RD WASH 5% HCl
 TAB VI

B. Investigation into DIBK-Aliquat 336 extraction procedure.

1. Preliminary. Various papers discussed the determination of gold in cyanide solutions and one (Groenwald, Analytical Chemistry, Vol. 40, No. 6, May 1968, reference (1) discusses the use of diisobutyl ketone with Aliquat 336 of General Mills (a Quarternary amine, tri octyl-methyl ammonium chloride), the gold being in the +1 oxidation state and in the basic range.

A subsequent paper by the same author (2), investigates the use of the tertiary amine, Alamine 336, General Mills (tri octyl amine) and Aliquat 336 for gold in +3 oxidation state and in either an aqua regia or a cyanide media. Groenwald recommend that in the pH range 0-4 the solution should be made 0.5 M sodium chloride, and in the pH range 4-10, the solution should be made 10^{-2} M cyanide and 0.1M in sodium chloride, and extracted into DIBK contain in 1% W/V Aliquat 336. The use of sodium chloride in the first instance appears to have been needed to insure the complete extraction of gold and to reduce the quantity of Aliquat 336 needed. In the second instance the sodium chloride was used to facilitate clarification of the phases. In the above papers the actual procedure for the extraction from aqua regia was not given, the analytical data given being for a cyanide media. Accordingly it was determined to investigate this procedure.

2. Discussion of the effect of salt concentration in the aqueous phase. From the earlier experiments discussed in Part A. and the general literature, it was apparent that the salt concentration has a significant and complex effect on the analysis altering the distribution of the gold between the organic and the aqueous phases, and thus concentration. Two of the known principals involved are the common ion effect, and the Setchenow salt effect, discussed by Groenwald, Analytical Chemistry, Vol. 43, No. 12, October, 1971, reference (3)..

The first has primarily a tendency to alter the distribution between the organic and the aqueous phase, and both the first and the second have an effect on the solubility of the organic phase.

From (3), the equation for the mutual solubility between organic phase and aqueous phase is developed in terms of the concentration of a material in comparison with what the concentration would have been if there had been no solubility, as follows:

$$\frac{C_{o/a} - C_o}{C_o} = \left[\left(1 - \frac{D_o \cdot S_{ao}}{100 D} \right) / \left(1 - \frac{D_a \cdot S_{oa}}{100 D_o} \right) \right] - 1$$

Where:

- $C_{o/a}$ = Concentration of material in organic phase.
- C_o = Concentration of material in organic phase if there had been no solubility.
- D_a & D_o = Densities, gram/ml of the aqueous and organic phases.
- S_{ao} = Solubility (%W/W) of aqueous in organic.
- S_{oa} = Solubility (%W/W) of organic in aqueous.
- $R_a \rho$ = V_a/V_o

The equation for the Setchenow salt effect which is:

$$\log \frac{S_{oa}}{S_{os}} = \log f = K_s C_s$$

Where S_{a0} is the solubility of the non-electrolyte in pure water, S_{0s} is the solubility of the non-electrolyte in the aqueous salt solution, f is the activity coefficient, C_s is the molar concentration of the salt in the aqueous phase, and K_s is the Setchenow salt coefficient.

Tables of solubility and Setchenow constants are given from which the calculations can be made.

An equation is developed for the relationship of the effect of a salt concentration (other than the analyte material) in terms of concentration of the analyte material in comparison with a standard.

This last equation would of course, permit calculation of the variation between the analyte material and a standard but for the fact that this is what is unknown.

As it is, it shows the possible variation, or relative error, due to assumed differences calculated from the solubility data provided. It is as follows:

$$\text{Relative error} = \frac{C_{o/s} - C'_{o/s}}{C'_{o/s}} = \frac{R_{a0} S_{0a} (D_s 10^{-K_s C_s} - D'_s 10^{-K_s C'_s})}{100 D_o - D_s R_{0a} S_{0a} 10^{-K_s C_s}}$$

Where $C_{o/s}$ = Concentration of a material in an organic phase in contact with a charged salt phase (that is, the concentration of the analyte).

$C'_{o/s}$ = Concentration of the material in an organic phase in contact with the aqueous phase (that is concentration of the standard).

C_s & D_s = Concentration and densities of charged salt phase (unknown).

C'_s & D'_s = Concentration and densities of salt concentration in standard.

All of the above equations are developed by simple mathematics, given some basic equations and assumptions.

From study and testing of these equations it is apparent that the greater the difference between the concentration of the salt in the unknown and the standard, the greater will be the error in determination. When there is a match the error should be zero, and as the ratio of volumes ($R_{a0} = V_a/V_o$) increases, the error changes rapidly. The calculation also shows that the higher the salt concentration, the less effect a difference makes. The graph, Tab VII, taken from reference (3) shows these relationships for one solvent, ethyl ether. Also given is the solubility data for MIBK & DIBK.

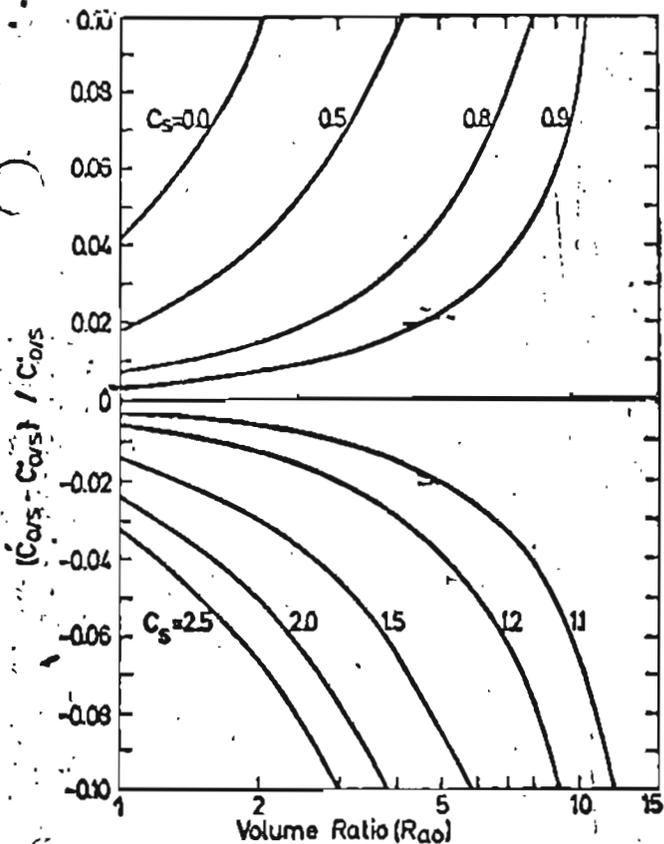


Figure 3. Influence of the Setchenow salt effect

Solvent: Ethyl ether
Salt: NaCl ($C'_s = 1.0M$)

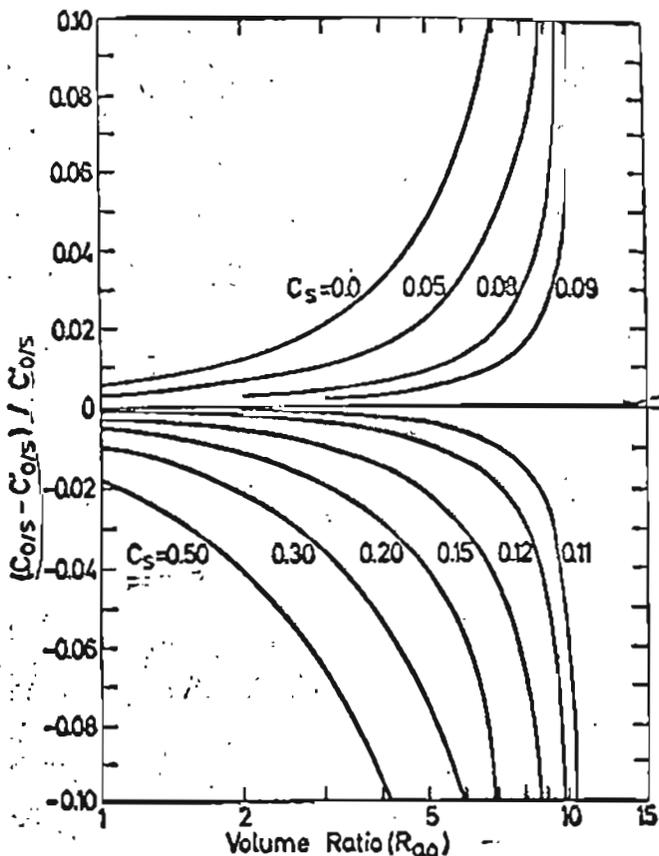


Figure 4. Influence of the Setchenow salt effect

Solvent: Ethyl ether
Salt: NaCl ($C'_s = 0.1M$)

NOTE: C'_s = Standard Salt Concentration

C_s = Unknown Salt Concentration

$$\frac{C_{o/s} - C'_{o/s}}{C'_{o/s}} = \text{Relative Error}$$

$$R_{ao} = V_a/V_o = \text{Volume Ratio}$$

From Solubility table:	MIBK	DIBK
S_{oa} (% W/W)	1.7	.06
S_{ao} (% W/W)	1.9	0.45
D_o (gm / ml)	.7985 (25°C)	.8089 (20°C)

If we consider the relative error $(C_{O/S} - C'_{O/S} / C'_{O/S})$ in terms of its congruent ratio, that is the total salt molarity, $C_S - C'_S / C'_S$ and add enough salt to increase both the unknown and the standard by "X" molarity.

$$\frac{C_S + X - (C'_S + X)}{C'_S + X} = \frac{C_S - C'_S}{C'_S + X}$$

And $C_S - C'_S / C'_S + X$ (or the relative error) is always smaller in absolute value than $C_S - C'_S / C'_S$.

The graph also shows the large influence of volume ratios, this factor, however, can easily be matched between unknown and standard.

3. Other factors or probable effects. From the papers referred to there seems to have been no interferences noted from other elements though many are extracted. The observations in the papers are of CN^- complexes. From preliminary experiments with MIBK, it was expected some interference from iron might be found, and should be investigated.

Groenwald concluded that the amount of Aliquat 336 needed to bring about complete extraction decreases with increasing salt concentration and a decrease in pH, that is if the salt content was kept up to 2 molar, the AQ 336 needed could be decreased to .01% (W/V) without significant effect. It was also determined that the addition of NaCl also has the effect of assisting in clarifying emulsions.

C. Conclusions.

The experimental and theoretical data would indicate that the best method would choose the solvent with the lowest solubility, duplicate the salt contents between standard and unknown as much as possible, and match the volume ratio. Since it is probably impossible to match salt concentrations, the larger the known salt concentration which can be added to each will minimize this difference.

Accordingly, first, since DIBK has the lowest aqueous solubility it should be the best solvent, and 1% W/V Aliquat 336 should be sufficient if salt molarity is kept high. Second, an equal amount of high molarity NaCl should be added to both unknown and standard, whether in solid or liquid. The amount being a compromise of ease of handling and volumes desired.

D. Experimental Analytical Procedure.

1. Technique.

- a. Digest 10 grams of sample in aqua regia by any standard method, make up to a known volume, centrifuge and take an appropriate aliquot.

- b. For every 50 ml of digestate add 10 ml of saturated salt solution (about 6 M).
- c. Extract in 10 ml DIBK with 1% (W/V) Aliquat 336.
- d. Estimate by AA analysis against standards extracted in a similar fashion.

2. Tests.

- a. To test solubility of DIBK in aqua regia solution, 100 ml of acid saturated DIBK was placed in a separating funnel with 500 ml of 33% aqua regia and 100 ml of 6 M NaCl, agitated for 10 minutes and phases measured after separation. There was no measurable change in volume of DIBK or aqueous solution.
- b. To test for the interference of iron many tests were run. Ref. (1) & (2) indicate no interference with iron as a CN ion. Others report the use of 25 ml of 40% tartaric acid to complex the iron prior to adjusting the pH to 4-5 and cyaniding and then extracting with DIBK-AQ 336.

Accordingly a large number of tests were run using various combinations of iron, gold and complexing agents, tartaric acid, ascorbic acid, citric acid, and various combinations of washings. The preliminary conclusions were that iron did increase the apparent absorption due to gold, and that tartaric acid did tend to compensate for the increased absorption. These results were subsequently determined to be misleading and possibly erroneous, and the data will not be included here, but in order to possibly prevent others from duplicating the same error, the following results were found.

1. When there was iron present but no gold, there was an apparent absorption of about 1.5 percent, that was not altered significantly by addition of tartaric acid before extraction.
 2. When there was iron present but also gold, the absorbance was increased by about 1.5 percent, but the prior addition of 30 ml of 40 percent (W/V) tartaric acid appeared to reduce this to approximately the correct absorption.
 3. In all cases the iron could be removed by one washing with 20 ml of 40 percent tartaric acid.
 4. The use of ascorbic or citric acid roughly duplicated the results of tartaric acid.
- c. To test further the effects of iron and the possible effect of a Deuterium arc background corrector, two sets of tests were conducted at different levels of gold, with and without iron and with and without tartaric acid:

PERCENT ABSORPTION

	Au PPM	No Fe No Tar.	Fe, No Tar.	No Fe + Tar.	Fe + Tar	Two Wash 15 ml Tar.
		(*)				
Uncorrected	.5	5.15(9)	5.83(9)	4.67(9)	5.48(9)	5.20(4)
D ₂ Arc Corr.	.5	4.47(9)	4.50(9)	4.34(9)	4.33(9)	4.52(4)
Uncorrected	4	37.06(5)	37.65(4)	35.94(5)	36.86(5)	- - - -
D ₂ Arc Corr.	4	35.54(5)	35.45(4)	34.58(5)	34.92(5)	

(*) Indicates number of replicate samples, the maximum deviation from the mean in any reading in all above data was .7% absorption.

From the above it appears that there is a flame absorption enhancement (background absorption) caused by iron and that it can be compensated for by use of a Deuterium background corrector. Also, the use of tartaric acid before the extraction merely depresses the absorption due to gold so that any resultant compensation for the enhanced flame absorption effect is purely coincidental. The use of tartaric acid as a wash was is effective in removing the iron, but whether it actually results in correct readings in this case is problematical. For high accuracy in low concentration analysis it would appear to be acceptable to wash both the unknown and the standard in the same way in order to eliminate any effect of iron. It is noted that as such washings are performed, the emulsion problem increases as the NaCl is washed out, but that the washings are not effective if the tartaric acid also contains NaCl.

- d. Comparison of analysis with Fire Assay. It is noted that the sampling error in the case of gold samples of this character is so great as to make individual comparisons very erratic. In this comparison two total samples of over 1,000 grams were sized and separated by heavy liquid and the fractions were analyzed by the DIBK-AQ 336 method, then converted to calculated fractions and heads. The fire assays were necessarily run on the actual fractions and thus are an average of about 70 grams in the best cases, thus giving rise to a lack of complete assurance. Nevertheless, the general agreement seems remarkable.

COMPARISON FIRE ASSAY & DIBK-AQ 336 AA
Ounces per ton. (Figures in parenthesis indicate number of analyses)

FRACTION	SAMPLE 1		SAMPLE 2	
	Measured Fire Assay	Measured DIBK-AA	Measured Fire Assay	Measured DIBK-AA
- 10 mesh				
Heads	1.57(6)	1.93(8)	.85(5)	1.17(8)
Calculated		1.79		.87
-10 +20				
Whole	1.87(2)	1.56(4)	.87(2)	.68(4)
-20 +35				
Float	.37(2)	.38(2)	.08(2)	.08(2)
Sink	- - -	12.08(3)	- - -	19.26(3)
-35 +65				
Float	.09(2)	.16(2)	.02(2)	.02(2)
Sink	- - -	46.13(3)	- - -	25.40(3)
-65 +200				
Float	.05(2)	.05(2)	.01(2)	.01(2)
Sink	- - -	37.42(3)	- - -	14.60(3)
-200				
Float	.10(2)	.15(2)	.03(2)	.05(2)
Sink	- - -	13.99(2)	- - -	5.86(2)

II. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions. It is believed that this is a highly accurate, precise method of analysis for gold, suitable for any purpose except very high ores, concentrates or bullion. It has the following advantages.

1. It can be used very easily as part of an overall assay for Cu, Pb, Zn, Ni, etc.
2. It is highly suitable for assay of liquids or materials which digest easily, such as amalgams.
3. It affords accuracy in determining amounts of gold in very small quantities, those that would be too small to weigh accurately on a bead balance.
4. By careful matching of salt concentration and volume ratios between unknown and standards, a very large sample size can be used, thus affording large concentrations and ability to analyze for gold into the parts per billion range.
5. It can be used in conjunction with fire assaying in eliminating the parting step in the determination of gold, in that the dore bead can be dissolved in aqua regia and run directly.

It has the following possible disadvantages:

- a. There has been no thorough test of interferences. Other elements may possibly interfere, and even the interference of iron has only been tentatively investigated.
- b. The technique has not been tried on a wide variety of material, and insufficient control tests have been made.
- c. If the first run of the extracted DIBK exceeds the range of the standards, it may be necessary to re-run with a smaller amount of aqueous phase. Attempts to make DIBK dilutions gave erratic results, possibly through poor mixing.

B. Recommendations

1. It is recommended that a large number of samples of different varieties of ore be run against fire assays.
2. That further study of interferences be made, including further confirmation of the corrective effect of the D₂ corrector.

C. Recommended Analytical Procedure

1. Digest 10 grams of sample in aqua regia, evaporate to approximately 35 ml, and make up to 100 ml liquid with deionized water (allow for estimated volume of undigested pulp, for example in a silica ore make up to about 103.3 ml).
2. Centrifuge. Take an appropriate aliquot, (according to convenience and estimated tenor of the material) and place in a container with a screw cap. For example, take 35 ml of digestate and place in a 25 x 200 mm culture tube with a screw cap and teflon liner.
3. Add 7 ml saturated NaCl solution and 7 ml of DIBK with 1% (W/V) Aliquat 336. (Vary as desired to suit tenor of ore and capacity of container). Shake one minute, allow phases to separate and run on AA against standards prepared the same way.
4. If iron present and resultant error can not be estimated, or correction is desired and it is available, use D₂ corrector. If not available, it is possible the same correction can be obtained through correction against a nearby non-absorbing line, 2477.

BIBLIOGRAPHY

1. Groenewald, Theo, *Analytical Chemistry*, Volume 40, No. 6, May 1968.
2. Groenewald, Theo, *Analytical Chemistry*, Volume 41, No. 8, July 1969.
3. Groenewald, Theo. Note, *Analytical Chemistry*, Volume 43, No. 12, October 1971.