Polarographic trace analysis of copper, lead and cadmium

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POLAROGRAPHIC TRACE ANALYSIS
OF
COPPER, LEAD AND CADMIUM

A Thesis
Presented to
The Graduate Faculty of the Department of Chemistry
University of Pacific

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by

Donald Paul Jepson
July 1973
This thesis, written and submitted by

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Dated Sept 17, 1973
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CHAPTER I

PROBLEM

The area of study for this project was the development of an accurate, reliable, and inexpensive method of trace analysis for copper, cadmium, and lead in foods. At this time, the Association of Official Analytical Chemists Manual, eleventh edition, (4) has the only official and recognized methods of analysis for copper (25.023), cadmium (25.018), and lead (25.041). In general, these procedures are long and tedious. The digestions involved often require many hours and are quite dangerous due to leakage of metallic and organometallic fumes from the digestion apparatus. The official methods of analysis for these elements require a very large outlay of money for special equipment and reagents.

It was the purpose of this project to determine the following:

A. The feasibility of using polarographic detection for copper, cadmium, and lead in trace amounts.

B. Find a new method of sample decomposition to replace the present digestion methods.

C. Study the possible uses of dithizone solutions as extraction and selection media prior to polarographic detection.

D. Develop a method of simultaneous polarographic
detection of copper, cadmium, and lead.
CHAPTER II

INTRODUCTION

The first portion of this chapter describes the historical development of polarography. This is followed by a discussion on applications of polarographic analysis. The chapter is concluded with a section on the evaluation of various methods of polarographic quantitative analysis.

I. HISTORICAL DEVELOPMENT

The first polarograph was developed in 1921 by Professor Jaroslav Heyrovsky at Charles University in Prague, Czechoslovakia (13). Although Heyrovsky had done a great deal of work in this area, it was not until 1934 that a major breakthrough was made by Ilkovic (13). Until that time, the basic theory and limitations of polarography were not at all well understood. Ilkovic was able to derive an equation which explained the theory of polarographic measurements mathematically.

\[
C = \frac{I_d}{k_n D^{1/2} m^{1/2} t^{1/2}}
\]

This in turn enabled him to make quantitative analyses using the relationship of concentration to the average diffusion current. The Ilkovic equation is still considered the
cornerstone of quantitative polarographic analysis.

Shortly after the introduction of the Ilkovic equation, I. M. Kolthoff and J. J. Lingane began doing a vast amount of research and development using the newly discovered theory of Ilkovic's (13, 15). The work jointly done by these two men has greatly increased the usefulness and popularity of polarography. At the present time polarography is a very popular area of scientific study. Approximately 1500 papers each year are being written in various areas dealing with polarographic analysis.

II. METHODS USED IN QUANTITATIVE POLAROGRAPHIC ANALYSIS

There are presently four popular methods of polarographic quantitative analysis (22, 17). They are as follows: The Pilot Ion Method; Wave Height-Diffusion Method; The Absolute Method; and the Standard Additions Method.

In the Pilot Ion Method of analysis, a ratio of the wave heights was found between two different metals at given concentrations. Then a second determination was made on a solution containing a given amount of one metal and containing an unknown amount of the other metal. From a comparison of wave heights one was able to determine the concentration of a given metal in the unknown solution.

This was a very uncomplicated technique because the wave height ratio is independent of the most troublesome
variables, i.e.; temperature, supporting electrolyte concentration, and capillary characteristics (17). It was decided not to use this technique even though it looked like the most foolproof method. The problem was the fact that the relationship \( I_d/C \) was assumed to be a linear function and at concentrations of \( 10^{-5} \text{M} \), or less this assumption is not always true. The relationship of \( I_d/C \) was a linear function at higher concentrations, but at lower concentrations \( I_d/C \) varied in a nonlinear manner. It was possible to make accurate measurements in a very narrow concentration range but this would be a very difficult situation to work with when one considers the practical application of this method in a control laboratory.

The Absolute Method (22) involved solving the Ilkovic equation to determine quantitatively the concentration of metal ions present. The Ilkovic equation is

\[
I_d = k \cdot n \cdot D^{\frac{1}{2}} \cdot C^{\frac{1}{2}} \cdot m^2 \cdot t^6
\]

Where

- \( I_d \) = Average diffusion current in mmamps
- \( n \) = Number of electron equivalents per molar unit
- \( D \) = The diffusion coefficient (sq. cm. per second)
- \( C \) = Concentration in millimole/liter
- \( m \) = Rate of mercury flow from electrode mg/sec
- \( t \) = Drop time in seconds
- \( k \) = Constant = 607 at 15\(^\circ\) to 40\(^\circ\)C.
the equation was solved for the concentration of reducible ions present.

\[ C = \frac{I_d}{k n D^{1/2} m^{1/2} t^{1/4}} \]

The sources of error in this method were due mainly to the accuracy of the measurements \( m, t, \) and \( I_d \). If the drop time was smaller than 2.0 seconds convection of the solution may have taken place and erroneous results occurred (15). The Absolute Method of Analysis was not selected for this work because of the non-linear relationship of \( I_d \) to \( C \) at concentrations less than 0.02\% (17). In this problem a method was needed which would detect concentrations in the range of 0.0005\% to 0.000002\% of reducible ion in solution. If the relationship of \( I_d \) to \( C \) is not linear below the 0.02\% level the results obtained would be misleading.

The third method of analysis which was used to determine concentrations of reducible ions quantitatively was the Wave Height-Diffusion Method (22). This is a graphic method (see Figure 1). A series of polarograms was made of a metal at different known concentrations (see Figure 2). The diffusion current, \( I_d \), was determined for each concentration by extending a line through the residual current portion of the wave, and measuring the distance between this extended line and the diffusion current portion of the polarogram. A plot was made then of each diffusion current value with
FIGURE 1

DETERMINATION OF $E_{\frac{1}{2}}$ and $I_d$

.001M Pb in .2N KCl

$E_{\frac{1}{2}} = -.38$  $I_d = 130$ mma

Volts

Current mma
FIGURE 2

CONCENTRATION VS. WAVE HEIGHT

Lead Solutions in .1M KCl and .02% Triton X-100
its corresponding concentration (see Figure 3). This plot should be a straight line relationship. However, the plot may be non-linear if the concentration of reducible ion is less than 0.02% of the solution (14).

A polarogram was made on a solution containing an unknown concentration of the metal to be detected. The plotted value of the diffusion current was compared to the Diffusion Current-Concentration Figure (see Figure 3). The concentration of the metal was quickly determined from the standard curve by visual inspection (15).

This method was not satisfactory for projected use as a method of detection in this project because a standard plot of diffusion current versus concentration would have to be made prior to each analysis to prevent error due to changes in drop time, mercury flow, and capillary action.

The fourth method of quantitative analysis was the Standard Additions Method (22). A solvent blank containing the supporting electrolyte and maximum suppressor was polarographed as a reference. After the solution was polarographed, known increments of each metal being detected were added and another polarogram made. This procedure was done as many times as needed to form a Diffusion Current-Concentration Curve (see Figure 4). A solution containing unknown amounts of the metals to be detected was polarographed and the wave heights compared to the Diffusion Current-Concentration Curve which was just made. The concentrations
When the $I_d$ is plotted with respect to concentration, the following result is observed. This plot may be a standard curve and polarograms of unknowns may be analyzed and compared to this curve.
FIGURE 4
STANDARD ADDITIONS FOR UNKNOWN

Cu 9.0 mg
Pb 30.0 mg
Cd 15.0 mg

Cu 6.0 mg
Pb 20.0 mg
Cd 10.0 mg

Cu 3.0 mg
Pb 10.0 mg
Cd 5.0 mg

Sample of unknown

Blank

Current (ma)
of each metal were easily interpreted from the plots (see Figures 5-7). Figures 5-7 represent the individual diffusion current versus concentration plots which were derived from Figure 4. These working curves were made at concentrations closely approximating the concentration of metal to be detected. These working curves should be made up once a week to insure accuracy.

This method was by far the best suited for the project's purpose because the method was not affected by the experimental variables which caused error in the other methods. Due to the fewer sources of error in this polarographic method, it was chosen as the means of quantitative detection. It is not the most popular method of detection, but was the best suited to the objectives of this project.
Unknown sample had an $I_d$ of 0.030 mma which corresponds to 2.3 mmg copper present.
Figure 6

LEAD--I_d Vs. CONCENTRATION

Unknown sample had an I_d of 0.04 mma which corresponds to 9.5 mg Pb.
Unknown sample had no detectable \( I_d \) for cadmium which indicates 0.0 \( \text{mmg} \) Cd present.
CHAPTER III

DISCUSSION OF TECHNIQUE

Chapter III contains a discussion of the sensitivity of the polarographic equipment employed in this project. Also appearing in this chapter is a discussion on detection levels and tolerances of heavy metals in natural products. It is concluded with a discussion on the use of dithizone to eliminate interference from ions naturally occurring in fish, turkey, shrimp, and rice.

I. SENSITIVITY OF POLAROGRAPHIC DETECTION

Theoretically, controlled potential polarographic trace analysis can be conducted on solutions as dilute as $10^{-7} \text{M.}$ (3, 9, 11). But in this case it was found most practical not to work below the $10^{-6} \text{M.}$ level. A problem arises in trying to detect metals at this level of concentration; the supporting electrolyte may contain up to 0.005% heavy metals as naturally occurring impurities. These heavy metals interfere with polarographic test results unless one of two things is done. The first was to remove the impurities by use of controlled potential electrolysis; the second remedy was to use 0.01N. or more dilute solutions of the supporting electrolytes. When 0.01N. solutions were used the amounts of impurities present were in the order of $1 \times 10^{-7} \text{M.}$, which was
about ten times smaller than the level of detection available with the polarograph used in this work. This meant that a solvent blank containing the electrolyte and suppressor still had to be run prior to each analysis merely as a safeguard in case of excessive amounts of impurities and to establish a reference.

Another problem area in polarographic trace analysis was the selection of the proper supporting electrolyte. Each electrolyte has a different effect upon a metal's reduction potential. By selection of the proper supporting electrolyte, one can separate or transpose the polarographic waves of two different metals. A good example of this phenomenon would be the polarographic curves of lead and cadmium. In a 1M. NaOH solution both metals have an $E_{1/2}$ value of about $-0.75V$. But in a 1M. KCl solution, lead has an $E_{1/2}$ value of $-0.40V$, while cadmium has an $E_{1/2}$ value of $-0.60V$. (17).

In this particular project, 0.01M. KCl was chosen as the supporting electrolyte because it gave a good separation between all three metal ions (17). The separation between copper, cadmium, and lead $E_{1/2}$ values was observed to be relatively good. See Table I. There was an adequate difference in $E_{1/2}$ potentials to resolve individual curves. When a wide separation existed between $E_{1/2}$ values, it was much easier to obtain a well resolved curve which would be evaluated. In this case, copper, cadmium, and lead were separated exceptiononly well with 0.01M. KCl so that a fairly large concentration
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<th>$E_1$ VALUES IN 0.01M. KCl</th>
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<tr>
<td>Copper</td>
<td>-0.20V.</td>
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<tr>
<td>Lead</td>
<td>-0.40V.</td>
</tr>
<tr>
<td>Cadmium</td>
<td>-0.60V.</td>
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of one ion would not interfere with the evaluation of one of the other ions.

II. DETECTION LEVELS OF Cu, Pb, and Cd

At the present time, the Food and Drug Administration tolerances allow for 5.0 ppm lead to be present in most food items such as flours, fruits, and fish. The action level for cadmium has not yet been established but estimates indicated a level of 0.5 ppm will be allowed (3). The copper level in food items has a tolerance for 100 ppm in meat and 50 ppm in vegetable items. The United States Public Health Service has established a very comprehensive guideline for determining water purity. The following tolerances were observed: Copper 1.0 ppm, Lead 0.05 ppm, and Cadmium 0.01 ppm (4).

For a method of detection to be useful it must be sensitive enough to detect amounts of a trace element present significantly below the official tolerance (1). In this project a screening method for determining the acceptability of various natural products and not necessarily the most accurate determination of metals present was being sought. This method needed only to detect levels of metals that were significantly lower than their given tolerances.

The polarographic instrument used in this project, a Heathkit EUA-19-2 polarograph module and accompanying
Heathkit dropping mercury electrode, is capable of detecting metals in solution at levels of $1 \times 10^{-6}$ M. concentrations. This meant that the final solution which contained the extracted heavy metals to be polarographed had to have at least a $1.0 \times 10^{-6}$ M. concentration so the instrument could give a reliable reading. The best theoretical detection level for this procedure is as follows. Consider an example:

Solution A contains $1 \times 10^{-6}$ M. of copper, lead, and cadmium. If the volume is 50 mls then this solution will contain 3.2 mmg copper, 10.3 mmg lead, and 5.6 mmg cadmium. Consider the conversion factor

$$1 \text{ ppm} = \frac{1 \text{ mmg ion}}{1 \text{ g sample}}$$

In this example, the detection level for each ion in a 1 gram sample would be

- **Copper** $\frac{3.2 \text{ mmg}}{1 \text{ gram}} = 3.2 \text{ ppm}$
- **Lead** $\frac{10.3 \text{ mmg}}{1 \text{ gram}} = 10.3 \text{ ppm}$
- **Cadmium** $\frac{5.6 \text{ mmg}}{1 \text{ gram}} = 5.6 \text{ ppm}$

These detection levels would not be satisfactory for this project because they were not sensitive enough to detect levels near or above the Food and Drug Administration action levels. The problem of lowering the detection level was overcome by simply increasing the amount of sample analyzed from 1 gram to 10 grams. When a 10 gram sample was used the detection level decreased as follows:
Copper \[ \frac{2.2 \text{ mmg}}{10 \text{ grams}} = 0.32 \text{ ppm} \]

Lead \[ \frac{10.2 \text{ mmg}}{10 \text{ grams}} = 1.03 \text{ ppm} \]

Cadmium \[ \frac{5.6 \text{ mmg}}{10 \text{ grams}} = 0.56 \text{ ppm} \]

The level of detection using a 10 gram sample was low enough to be satisfactory in meeting the requirements for screening methods as outlined earlier.

III. DITHIZONE EXTRACTION

In this project, it was found that natural products such as flour, shellfish, meats, and fish all contain concentrations of many elements which were detectable using polarographic analysis (5). This presented a serious problem because these metals and anions interfered with the waves produced by the copper, cadmium, and lead present. To remove these interfering ions, one must use a method of physical separation prior to polarographic analysis. There are four well accepted methods of separation available: Precipitation, Extraction, Chemical Reduction, and Electrolytic Reduction (17).

It was found that an extraction using dithizone was a good method easily adapted to this problem. By buffering and pH adjustment, one could remove most of the sources of interference that were found in natural products and water (20). The primary sources of interference that were mentioned above could be grouped into the following areas:
soluble earth elements, alkaline earth elements, rare earth metals, and anions which could be electrochemically reduced.

The dithizone extraction can be used in a similar manner. When a natural product was found to contain levels of copper, lead, or cadmium, which would have grossly interfered with the mutual determination, a second dithizone extraction would be done and the one ion at the higher concentration evaluated separately.
CHAPTER IV

EXPERIMENTAL PROCEDURES

In this study, samples of turkey muscle tissue, ling fish muscle tissue, shrimp, and rice were used to represent typical natural products (3). The following chapter describes how these natural products were evaluated for copper, lead, and cadmium.

I. PREPARATION OF SAMPLES

A sample was made by collecting ten 5 gram subsamples taken at random as pictured in Figure 8. The subsamples were blended in a Waring blender for one minute to obtain small particle size. 10 grams were placed on a cellophane sheet and dried in the vacuum oven at 120°F at 1.0 mm Hg pressure for sixteen hours. The dried sample was placed in a mortar and ground to a fine powder; then wrapped in filter paper to form a crude looking cigarette. The sample was either combusted or held in a desiccator for combustion at a later time.

II. COMBUSTION

50 ml of 1% nitric acid was added to a clean, dry 12 liter combustion flask (24, 10). The sample was placed in the platinum wire gauze basket of the combustion flask stopper and a small %" diameter dot of 1% methylene blue
Item to be Sampled

10-5 gram core samples are taken and combined.

Combined samples are blended.

10 grams of sample is weighed and dried in cellophane.

Dry sample is ground in mortar and wrapped in filter paper.
dye was stained on the corner of the sample. The basket and stopper were inserted in the combustion flask and held in place with a chromatography clamp. A gas delivery tube was inserted through the side arm and submerged in the 1% nitric acid solution. The flask was slowly purged with oxygen for two minutes, then the oxygen delivery tube was removed and the balloon quickly slipped over the side arm opening. The balloon was secured firmly with a rubber band to the side arm. The combustion flask was placed in a hood and the infrared igniter lamp was focused on the blue dot of the sample for ignition as demonstrated in Figure 9. When the last remaining ashes stopped glowing, the flask was removed from the hood and placed in the refrigerator for one hour. After cooling, the flask was swirled to coat the sides with nitric acid solution and then emptied into a funnel which filtered directly into a 250 ml separatory funnel. Two 50 ml aliquots of 1% nitric acid were used consecutively to rinse the combustion flask and these aliquots were added to the original trapping solution.
III. DITHIZONE EXTRACTION

The purpose of the dithizone extraction was to remove various ions which commonly occur in natural products but which interfered with ions that were being polarographed. Basically, the dithizone extraction separated the heavy metals which formed dithizone complexes (Fe, Hg, Zn, Sn, Co, Ni, Ag, Pb, Cd, and Cu) from the ions and metals which do not form dithizone complexes. In this case, copper, lead, and cadmium formed dithizone complexes while alkaline earth and alkali earth metals do not.

Dithizone complexes are quite pH-dependent (20); the pH at which a metal may be extracted from the aqueous phase is dependent upon the pK value of the metal-dithizone complex (6). By use of citrate as a masking agent and a pH of 9, the metals which formed dithizonates that would interfere (such as Fe, Sn, and Ni) were eliminated.

The nitric acid solution containing the burnt sample was treated with 5 mls of 10% urea solution and 5 mls of 40% hydroxyamine hydrochloride solution. These reagents deactivated any organic materials or partially burnt materials that broke down the dithizone and dithizone complexes which formed (10, 16). 5 mls of 1N ammonium citrate was added to the separatory funnel and ammonium hydroxide was added until the solution reached pH 9.0. 20 mls of chloroform and 1 ml of chloroform-dithizone
solution containing 1 mg of dithizone were added and the separatory funnel was shaken for one minute. After the two layers had fully separated the chloroform layer was drained into a 50 ml beaker. If the chloroform-dithizone layer was violet or red, the extraction procedure was repeated until the chloroform-dithizone layer remained blue. The red color in the dithizone layer indicated all of the dithizone was converted to metallic dithizonates of copper and lead. A blue dithizone layer indicated an excess of dithizone present. The extractions were combined and 5 ml of 1% nitric acid was added to the extract. The chloroform-dithizone extraction was evaporated to dryness using a hot plate. The dried dithizone extract was placed in a muffle furnace for 15 minutes at 300°C. The drying process converted the metals that were present in the chloroform-dithizone extract to inorganic nitrate salts. The beaker was removed from the muffle furnace and placed in a desiccator to cool. When cool, the sample was ready for polarography.
IV. POLAROGRAPHIC ANALYSIS

The polarographic cell used in this procedure was equipped with a platinum counter electrode. This arrangement permitted the utilization of a controlled potential to be applied to the cell. This principle increased the range of the potentials at which polarographs were made because the platinum electrode was capable of producing greater positive potentials without hydrogen gas evolution than the mercury electrode (24).

A solvent blank polarograph was recorded by using 50 mls of 0.002N KCl containing 0.002% Triton X-100. The blank was degassed with nitrogen for fifteen minutes. The polarograph module was set at 1 mma full scale deflection and 0.10 volt/minute sweep rate with the initial potential set at 0.00 volts (see page 30). The mercury column was set at 50 cm and the D.M.E. had an approximate drop time of 16 drops per minute. See diagrams (pages 31-33) for set up. After the polarograph of the blank was recorded, 3.0 mmg copper, 10 mmg lead, and 5.0 mmg cadmium were added simultaneously and the solution degassed again and a second polarograph was made at the same settings. A third polarograph was made after a second addition of ions. Finally, a fourth polarograph was made after a third addition of ions.

The beaker containing the sample was prepared for polarography by adding 50 mls of 0.002N KCl containing
Figure 10
POLAROGRAPHY MODULE AND RECORDER SET UP
Figure 12
FUNCTION DIAGRAM OF POLAROGRAPHY MODULE
SCHEMATIC OF THE
HEATH SCIENCE SERIES
POLAROGRAPHY MODULE
MODEL EUA-19-2

NOTES:
1. ALL RESISTORS ARE 1/2 WATT, UNLESS 250 MARKED OTHERWISE. RESISTOR VALUES ARE NORMAL: 1 K, 10K, 20K, 100K, 1 MOHm.
2. ALL RESISTORS ARE 1% TOLERANCE UNLESS MARKED OTHERWISE.
0.002% Triton X-100 suppressor and degassed for fifteen minutes with nitrogen. The sample was polarographed at the exact same settings and conditions as the blank.

V. SOLVENTS AND REAGENTS

The reagents and solvents used in the procedures described in this project are listed below along with the corresponding purity.

A. Reagents

3. Nitric acid, HNO₃, A.C.S. Grade.
4. Hydroxyaminehydrochloride, NH₂OH-HCl, A.C.S. Grade.
5. Urea, NH₂CONH₂, A.C.S. Grade.
6. Dithizone, diphenylthiocarbazone, A.C.S. Grade.
7. Ammonia, NH₃, A.C.S. Grade.
8. Ammonium citrate, (NH₄)₂HC₆H₅O₇, A.C.S. Grade.
10. Triton X-100, U.S.P. Grade.
11. Mercury, A.C.S. Grade, triple distilled.
13. Lead chloride, PbCl₂, A.C.S. Grade.
14. Cadmium chloride, CdCl₂·2½H₂O, A.C.S. Grade.
15. Copper chloride, CuCl, A.C.S. Grade.
16. Sulfuric acid, H₂SO₄, A.C.S. Grade.
17. Potassium dichromate, K₂Cr₂O₇, A.C.S. Grade.
B. Solvents

1. Chloroform, CHCl₃, A.C.S. Grade.

2. Water, demineralized to give a resistance greater than one megaohm.

C. Preparation of Solutions

1. 1% methylene dye solution-
   1 gram of dye was dissolved in 100 mls demineralized water.

2. 1% nitric acid solution-
   A 10 ml aliquot of nitric acid was diluted to 1000 mls in a volumetric flask with demineralized water.

3. 40% hydroxyamine hydrochloride solution-
   40 grams of hydroxyamine hydrochloride was dissolved in 100 mls of demineralized water.

4. 10% urea solution-
   10 grams of urea was dissolved in 100 mls of demineralized water.

5. Dithizone-chloroform solution-
   100 mg of dithizone was dissolved in 100 mls of chloroform. The solution was kept in a dark brown bottle under refrigeration. This solution was prepared fresh every two weeks.

6. 1.0 N. Ammonium citrate solution-
   22.6 grams of ammonium citrate was dissolved in demineralized water and diluted to 100 mls in a volumetric flask.
7. 2N. Potassium chloride stock solution-
149.1 grams of KCl was dissolved in water and
diluted to 1000 mls in a volumetric flask.

8. 0.02N. Potassium chloride working solution-
A 10 ml aliquot of the KCl stock solution was
diluted volumetricly to 1000 mls.

9. 0.01M. Copper standard stock solution-
0.2475g CuCl was placed in a 250 ml volumetric
flask. 20 mls of 6N. HCl was added to dissolve
the salt. The solution was diluted to 250 mls with
demineralized water.

10. Copper standard working solution-
5 mls of the copper stock solution was diluted to
1000 mls in a volumetric flask. Final concentration:
3.2 mmg/ml.

11. 0.01M. Lead standard stock solution-
0.6955 grams of PbCl₂ was placed in a 250 ml
volumetric flask. A small amount of water was
added to dissolve the salt, then diluted to volume
with demineralized water.

12. Lead standard working solution-
A 5 ml aliquot of the lead stock solution was
diluted to 1000 mls in a volumetric flask. Final
concentration: 10.3 mmg/ml.

13. 0.01M. Cadmium standard stock solution-
0.5710 grams CdCl₂·2½H₂O was placed in a 250 ml
volumetric flask. A small amount of water was added to dissolve the salt, then diluted to volume with demineralized water.

14. Cadmium standard working solution—
A 5 ml aliquot of the cadmium stock solution was diluted to 1000 mls in a volumetric flask. Final concentration: 5.6 mmg/ml.

15. Cleaning solution—
200 grams $\text{K}_2\text{Cr}_2\text{O}_7$ was weighed and dissolved in as small a volume of water as possible. 800 mls of concentrated sulfuric acid was carefully added to the $\text{K}_2\text{Cr}_2\text{O}_7$ solution.
CHAPTER V.

RESULTS

The procedures developed were found to be easy to use and adaptable to a great many control laboratory uses. The aspects which make this method very desirable are as follows:

A. The procedures will detect the three metals simultaneously.

B. The entire procedure will require only three hours of actual laboratory work.

C. Metals are typed according to $E_{\frac{1}{2}}$ potentials as well as evaluated for quantity present; thus avoiding a second set of confirmation tests.

A single standard analysis for lead required approximately four to eight hours to complete. This included digestion, extraction, complex formation, and detection. The procedure in this project reduced the work time to approximately three hours and the steps in this procedure were combustion, extraction, and detection. Better utilization of manpower was realized by using this method because analytical data was given on three metals simultaneously. In the Association of Official Analytical Chemists Handbook, eleventh edition, the official final action method of analysis for lead (one method 25.041) is a dithizone extraction method. This type of analysis
required a confirmation test (thin-layer chromatography plate) if unacceptable levels of lead were detected.

A series of experiments on the lead content in various natural products was done in which a sample was evaluated by the Official Final Action method and then by the method developed in this project. The results of the tests are listed in Table II. The data indicated that each method gave comparable results. Natural product samples of ling, shrimp, turkey, and rice were evaluated with the method developed in this project and the results may be seen in Figures 14-17 on pages 41-44.

The percent recovery of a metal from a natural product was a very critical area of concern when working on this project. A method is only reliable as long as a good recovery is obtained (3). To determine the amount of recovery in this procedure, a ten gram sample of ling fish was fortified with 3.0 mmg copper, 10 mmg lead, and 5,5 mmg cadmium. A second ten gram sample was prepared; the only difference was no fortification with copper, lead, or cadmium. The samples were analyzed and the data noted on Table III.

The data in Table III revealed that 2.8 mmg copper was recovered which was equivalent to 93.3% of the actual copper added to the sample, while the lead recovered was 8.6 mmg or 86.0% and the cadmium recovered was 5.0 mmg or 90.8%. The recoveries were desirable from the standpoint
TABLE II.
COMPARATIVE ANALYSIS OF NATURAL PRODUCTS

<table>
<thead>
<tr>
<th>Natural Products</th>
<th>Colorimetric Method</th>
<th>Polarographic Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ling</td>
<td>A 0.20 ppm</td>
<td>0.25 ppm</td>
</tr>
<tr>
<td>Ling</td>
<td>B 0.22 ppm</td>
<td>0.20 ppm</td>
</tr>
<tr>
<td>Ling</td>
<td>C 0.19 ppm</td>
<td>0.22 ppm</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>0.20 ppm</td>
<td>0.22 ppm</td>
</tr>
<tr>
<td>Shrimp</td>
<td>A 0.14 ppm</td>
<td>0.10 ppm</td>
</tr>
<tr>
<td>Shrimp</td>
<td>B 0.10 ppm</td>
<td>0.05 ppm</td>
</tr>
<tr>
<td>Shrimp</td>
<td>C 0.08 ppm</td>
<td>0.10 ppm</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>0.10 ppm</td>
<td>0.08 ppm</td>
</tr>
<tr>
<td>Rice</td>
<td>A 0.10 ppm</td>
<td>0.06 ppm</td>
</tr>
<tr>
<td>Rice</td>
<td>B 0.12 ppm</td>
<td>0.08 ppm</td>
</tr>
<tr>
<td>Rice</td>
<td>C 0.08 ppm</td>
<td>0.10 ppm</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>0.10 ppm</td>
<td>0.08 ppm</td>
</tr>
</tbody>
</table>
FIGURE 14
LING--NATURAL PRODUCT ANALYSIS

10 gram sample size
Cu 20.0 mng = 2.0 ppm
Pb 5.0 mng = 0.5 ppm
Cd 1.0 mng = 0.0 ppm
10 gram sample size

Cu 5.0 mg = 0.5 ppm
Pb 1.0 mg = 0.1 ppm
Cd 0.0 mg = 0.0 ppm
FIGURE 16

TURKEY—NATURAL PRODUCT ANALYSIS

10 gram sample size
Cu 0.0 mmg = 0.0 ppm
Pb 2.0 mmg = 0.2 ppm
Cd 0.0 mmg = 0.0 ppm
FIGURE 17
SHRIMP--NATURAL PRODUCT ANALYSIS

10 gram sample size

Cu 10.0 mmg = 1.0 ppm
Pb 1.0 mmg = 0.1 ppm
Cd 0.0 mmg = 0.0 ppm
## TABLE III.

**PERCENT RECOVERY FROM LING**

<table>
<thead>
<tr>
<th>Fortification level of sample</th>
<th>Copper (mmg)</th>
<th>Lead (mmg)</th>
<th>Cadmium (mmg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content in unfortified sample</td>
<td>1.2 mmg</td>
<td>0.4 mmg</td>
<td>0.0 mmg</td>
</tr>
<tr>
<td>Content in Fortified sample</td>
<td>4.0 mmg</td>
<td>9.0 mmg</td>
<td>5.0 mmg</td>
</tr>
<tr>
<td>Amount of fortification recovered</td>
<td>2.8 mmg</td>
<td>8.6 mmg</td>
<td>5.0 mmg</td>
</tr>
<tr>
<td>Percent recovery</td>
<td>93.3%</td>
<td>86.0%</td>
<td>90.8%</td>
</tr>
<tr>
<td>Amount of metal after recovery correction</td>
<td>1.23 mmg</td>
<td>0.46 mmg</td>
<td>0.00 mmg</td>
</tr>
</tbody>
</table>
of reliability because they were greater than 85.0%. This data indicated that an adjustment for recovery would have to be done on all samples that are evaluated by this method.

The following calculation was an example of how the raw data was manipulated to determine trace element content.

<table>
<thead>
<tr>
<th>Given:</th>
<th>Sample size:</th>
<th>10 grams</th>
<th>10 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level of Cu fortification:</td>
<td>3.0 mmg</td>
<td>3.0 mmg</td>
<td></td>
</tr>
<tr>
<td>Cu detected in sample:</td>
<td>0.30 mmg</td>
<td>2.9 mmg</td>
<td></td>
</tr>
<tr>
<td>% recovery:</td>
<td>86.7%</td>
<td>86.7%</td>
<td></td>
</tr>
<tr>
<td>Corrected Cu content:</td>
<td>0.34 mmg</td>
<td>0.34 mmg</td>
<td></td>
</tr>
<tr>
<td>ppm concentration:</td>
<td>0.034 ppm</td>
<td>0.034 ppm</td>
<td></td>
</tr>
</tbody>
</table>

Copper recovered from fortified sample:

\[ 2.9 - 0.3 = 2.6 \text{ mmg} \]

Percent recovery of copper:

\[ \frac{2.6 \text{ mmg} \times 100}{3.0 \text{ mmg}} = 86.7\% \]

Corrected copper content:

\[ \frac{0.3 \text{ mmg} 	imes 0.34 \text{ mmg}}{0.867} \]

Conversion of mmg to ppm:

\[ \frac{0.34 \text{ mmg} \times 1 \text{ ppm}}{10.0 \text{ g}} = 0.034 \text{ ppm} \]

This method of detection is very versatile and can
be expanded to include many metals besides copper, lead, and cadmium. Proper selection of the supporting electrolyte coupled with selective dithizone extractions make it possible to detect zinc, iron, bismuth, mercury, manganese and a host of other metals from one sample.
BIBLIOGRAPHY


