Glycol Formulations by Atomic Absorption Spectroscopy

The Determination of Aluminum, Copper, Iron, and Lead in

DOE/NASA CR-150520

DOE/NASA Contract Report

Prepared by

Gulf Research and Development Company

Under Contract NAS8-22235 with

Jet Propulsion Laboratory, California Institute of Technology

For the Department of Energy

Prepared for

George C. Marshall Space Flight Center, Alabama

National Aeronautics and Space Administration

FEB 1979
This report describes initial screening tests and the results obtained in developing procedures to determine Al, Cu, Fe, and Pb in glycol formulations. As little as 0.02 mg of carbon and 0.03 mg of Pb or Fe may be determined. A 1-mg sample of methyl isobutyl ketone (MIBK) was also extracted into thiocarbamate (DDC) into methyl isobutyl ketone (MIBK). Alumimum was also extracted into DDC and after comparison with emission spectroscopy, was selected for Al also. Before completion of carbon, copper, iron, and lead are extracted with diethylene thiocarbamatate (DDC) into methyl isobutyl ketone (MIBK). Alumimum may be determined as little as 0.2 mg. It is used in screening formulations as a chelating agent. As little as 0.02 mg carbon and 0.03 mg Pb or Fe may be determined. A 1-mg sample of methyl isobutyl ketone (MIBK) was also extracted into thiocarbamate (DDC) into methyl isobutyl ketone (MIBK). Alumimum was also extracted into DDC and after comparison with emission spectroscopy, was selected for Al also. Before completion of Al, Cu, Fe, and Pb, and after comparison with absorption spectroscopy, was due to determine Al, Cu, Fe, and Pb in glycol formulations. Atoms in absorption spectroscopy. Absorption spectroscopy was due to determine Al, Cu, Fe, and Pb in glycol formulations. Absorption spectroscopy.

This work was done under the technical management of John M. Caudle, Marshall Space Flight Center.
TABLE OF CONTENTS

I. Introduction ............................................. 1
II. Abstract .................................................. 1
III. Experimental and Results ......................... 2
IV. Discussion .............................................. 5
V. Conclusions ............................................. 6
VI. Recommendations .................................... 6

APPENDIX I (Method AA-9A) ......................... 7
APPENDIX II (Method AA-4D) ......................... 10
INTRODUCTION

The Research Analytical Department of the Corpus Christi Technical Center has been requested to develop procedures for the determination of low levels of aluminum, copper, iron, and lead in aqueous glycol formulations. It was hoped that the analysis of these solutions would permit monitoring of the extent of corrosion occurring in tests being carried out by Houston Chemical Corporation to evaluate various materials of construction for use in solar panel systems without requiring dismantling of the test panels for examination.

This report describes initial screening tests and the results obtained in developing procedures for Al, Cu, Fe, and Pb determinations in glycol formulations and in their application to a series of samples from preliminary corrosion tests.

II. ABSTRACT

This report describes initial screening tests and the results obtained in developing procedures for Al, Cu, Fe, and Pb determinations in glycol formulations and in their application to a series of samples from preliminary corrosion tests. The determination of Al, Cu, Fe, and Pb in glycol formulations has been requested to develop procedures for the determination of low levels of air, water, and Pb in glycol formulations.
An initial screening of a series of four glycol formulation samples was performed by filtering solids from the samples and diluting the filtrate (5 ml to 50 ml) with deionized water. The diluted solutions were read for Cu, Fe, Pb, and Al on the AA spectrophotometer. The solid portions of these samples were then fired on the emission spectrophotograph to obtain a qualitative analysis of the elements present. The results of these determinations are presented in Table I.

### TABLE I

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Cu, mg/l</th>
<th>Fe, mg/l</th>
<th>Pb, mg/l</th>
<th>Al, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-6076 Residue From I-6070 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6077 Residue From I-6071 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6078 Residue From I-6072 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6079 Residue From I-6073 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

Following the initial screening determinations it was decided to develop extraction procedures to remove the metal ions from their glycol matrix and to concentrate the metal solutions to remove the glycol matrix and to concentrate the metal solutions prior to their analysis. Cu and Pb appeared to be the most suitable for AA determination so a procedure was developed in which the cations are complexed with DTPA and the metals are extracted into a Merck phase then read on the AA spectrophotometer. This procedure was applied to data collected from the static and dynamic tests and the results are presented in Table III, together with the weight loss results from the corrosion tests.

### TABLE III

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Cu, mg/l</th>
<th>Fe, mg/l</th>
<th>Pb, mg/l</th>
<th>Al, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-6076 Residue From I-6070 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6077 Residue From I-6071 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6078 Residue From I-6072 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6079 Residue From I-6073 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

### TABLE II

The results of the emission spectrophotographic determinations are presented in Table II.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Cu, mg/l</th>
<th>Fe, mg/l</th>
<th>Pb, mg/l</th>
<th>Al, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-6076 Residue From I-6070 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6077 Residue From I-6071 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6078 Residue From I-6072 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6079 Residue From I-6073 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

### TABLE I

The results of the emission spectrophotographic determinations are presented in Table I.

<table>
<thead>
<tr>
<th>Concentration (mg/l)</th>
<th>Cu, mg/l</th>
<th>Fe, mg/l</th>
<th>Pb, mg/l</th>
<th>Al, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
</tr>
<tr>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
</tr>
<tr>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
</tr>
</tbody>
</table>

### TABLE II

The results of the emission spectrophotographic determinations are presented in Table II.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Cu, mg/l</th>
<th>Fe, mg/l</th>
<th>Pb, mg/l</th>
<th>Al, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-6076 Residue From I-6070 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6077 Residue From I-6071 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6078 Residue From I-6072 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>I-6079 Residue From I-6073 Before Static Test</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

The results of the emission spectrophotographic determinations are presented in Table I.

<table>
<thead>
<tr>
<th>Concentration (mg/l)</th>
<th>Cu, mg/l</th>
<th>Fe, mg/l</th>
<th>Pb, mg/l</th>
<th>Al, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
</tr>
<tr>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
</tr>
<tr>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>&gt;5</td>
</tr>
<tr>
<td>Sample</td>
<td>Description</td>
<td>Ph</td>
<td>( \text{mg/l from mg from Fe} )</td>
<td>( \text{mg/l from mg from Fe} )</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>----</td>
<td>---------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>4.4</td>
<td>160925 Exposed</td>
<td>0.007</td>
<td>0.000 0.10</td>
<td>0.000 0.10</td>
</tr>
<tr>
<td>4.3</td>
<td>160925 Unexposed</td>
<td>0.000</td>
<td>0.000 0.10</td>
<td>0.000 0.10</td>
</tr>
<tr>
<td>8.8</td>
<td>160933 Exposed</td>
<td>0.002</td>
<td>0.000 0.10</td>
<td>0.000 0.10</td>
</tr>
<tr>
<td>8.3</td>
<td>160933 Unexposed</td>
<td>0.000</td>
<td>0.000 0.10</td>
<td>0.000 0.10</td>
</tr>
<tr>
<td>11.3</td>
<td>160922 Exposed</td>
<td>0.002</td>
<td>0.000 0.10</td>
<td>0.000 0.10</td>
</tr>
<tr>
<td>11.8</td>
<td>160922 Unexposed</td>
<td>0.000</td>
<td>0.000 0.10</td>
<td>0.000 0.10</td>
</tr>
</tbody>
</table>

Results of CCT Method AA-4B end Sample Weight Loss for Accelerated Corrosion Test.

Table III
The negative value shown for Fe in the "mg fort Analysis" column indicates that the solutions actually lost Fe concentration during the test. The "mb fort Ott. Loss" column shows the amount of metal lost from the corrosion coupons during the tests and should equal the "mg fort analysis" column for a given pair of samples if all the material lost from the coupons was recovered in the solution analysis. No significant amount of solids was present in any of these samples as presented for analysis, although it is understood that solids were scrubbed from the corrosion coupons after the exposure and were discarded prior to reweighing the corrosion coupons to determine weight losses.

It was observed in developing procedure CC'TC-40 that the efficiency of extraction of the metal ions into the M13K phase was strongly dependent on the glycol concentration of the aqueous phase. As the glycol content of the aqueous phase increases, the chelated metal ion distribution shifts toward the aqueous phase during the extraction. For this reason it is very important to establish calibrations for each sample dilution by making an appropriate standard addition.

Aluminum is reportedly most sensitively determined by emission spectroscopy. Accordingly, an initial attempt was made to determine aluminum in glycol by chelating into Caro's potassium tert-chloride with 8-hydroxyquinoline and evaporating the M. onto NaCl which was subsequently fired in the emission spectrograph. This procedure yielded no significant correlation of aluminum content with emission spectrographic results. Therefore, an initial attempt was made to determine aluminum by emission spectrographic analysis. It was observed that the absorbance of aluminum in glycol was increased by the addition of an internal standard, such as the calcium ammonium nitrate used in Table IV.

Next, aluminum in 40-mL portions of 50% ethylene glycol formulation was chelated with 8-hydroxyquinoline and extracted into MIBK. This extract was then read directly on the AAS spectrophotometer and, after addition of chromium as an internal standard, the absorbance was measured to determine the aluminum concentration. Results are presented in Table IV.

<table>
<thead>
<tr>
<th>Added (mg/L)</th>
<th>AAA Response</th>
<th>Emission Spectroscopic Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.001</td>
<td>2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.5</td>
<td>1.63</td>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>2.0</td>
<td>3.4</td>
<td>3.2</td>
</tr>
<tr>
<td>4.0</td>
<td>3.2</td>
<td>4.2</td>
</tr>
</tbody>
</table>

While the AA response for Al shown in Table IV is weak, it is clearly preferable to the emission spectrographic responses. Accordingly, a procedure involving the completion of 155 extracts for Al was developed (CCTC Method AA-9A) and applied to the same series of samples presented earlier in Table II. The results of this application are shown in Table V.

**TABLE V**

Comparison of Emission Spectroscopic and AA Results for Al in MIBK Extracts

<table>
<thead>
<tr>
<th>Conc. of Al (mg/L)</th>
<th>AAA Response</th>
<th>Emission Spectroscopic Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.001</td>
<td>2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.5</td>
<td>1.63</td>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>2.0</td>
<td>3.4</td>
<td>3.2</td>
</tr>
</tbody>
</table>

The negative value shown for Fe in the "mg fort analysis" column indicates...
The limits of detection varied for Al standards in Table V reflect different recovery efficiencies of Al standard additions made to various samples to establish recovery efficiencies of Al standards. Although general trends are reflected in Table V, the results do not reflect definite losses or gains in the metal contents of the solutions.

In general, the physical loss from the coupons could not be detected, although the loss from the extraction media and the reason for the observed losses are not known. The reasons for the observed losses are not clear, although the differences in detection limits for the various samples may reflect differences in recovery efficiencies. The differences did not appear to be related to the glycol content in the extraction media.

IV. DISCUSSION

Tables III and V show there is very little correlation between the weight losses observed for the corrosion coupons and the dissolved metals found in the corrosion test fluids. Further, the fact that very few solids were present in the corrosion test fluids suggests that the tests were performed in the absence of solids.

The results of the accelerated corrosion tests are shown in Table V. The weight loss, % from Analysis, mg from Sample, and % from Table V, mg from Analysis, are shown for each sample. The weight losses are given as mg from Solution, mg from Sample, and mg from Analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Table V, mg from Table V, mg from</th>
<th>% from Sample</th>
<th>% from Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As pointed out for Table III, the weight losses observed from corrosion coupons are not connected to the glycol content in the extraction media and the reason for the observed losses is not known. The reason for the observed losses is not known.
corrosion products in test fluids might offer a means of monitoring the progress of corrosion during tests. Discussions with the technician who performed the accelerated corrosion tests indicate that most of the corrosion products adhered to the test coupons and were washed and scrubbed free (and discarded) prior to taking final weights of the coupons.

The data in Tables III and V suggest that Cu, Fe, Pb and Al may have low solubilities in many aqueous glycol solutions. This is particularly true for Fe which apparently actually dropped out of solution during the test. Fe appears to be more soluble in the essentially pure glycol formulation sampled before the test than in the aqueous solution sampled afterward. Cu appears to be an exception to the low solubility in aqueous solutions indicated for the other elements, being soluble in the aqueous propylene glycol formulation and to a lesser extent the aqueous triethylene glycol formulation. It should be mentioned that a pure ethylene glycol formulation stored in a metal container was found to contain 3.5 mg/l Pb, indicating considerable solubility of lead in the pure glycol. Similar formulations stored in plastic all contained less than 0.1 mg/l Pb.

V. CONCLUSIONS

1. There is little correlation between corrosion of metal test coupons and analysis of test fluids.
2. Most corrosion products must have remained on or near the actual site of corrosion until physically removed during cleanup.
3. Cu at levels down to 0.02 mg/l and Fe and Pb at levels down to 0.06 mg/l in glycol formulations can be determined by extraction into MIRK with diethyldithiocarbamate and AA completion (CETC Method A-9). Al at levels as low as 0.3 mg/l in glycol formulations can be determined by extraction into MIRK with 8-hydroxyquinoline followed by AA completion (CETC Method A-9).

VI. RECOMMENDATIONS

1. Little confidence should be placed in the analysis of test fluids as a means of evaluating the extent of metal corrosion during tests.
2. Solids obtained from test fluids during corrosion tests should be weighed and analyzed qualitatively by emission spectroscopy and, when the amount and nature warrant, they should be digested and analyzed quantitatively by emission spectroscopy and when the amount and nature warrant, the corrosion products should be weighed and analyzed quantitatively.
3. Corrosion products must be removed during cleanup of metal coupons.
4. There is little correlation between corrosion of metal test coupons and analysis of test fluids.

Charles L. Kolikoff
Research Chemist
As little as 0.3 mg/l Al can be determined in aqueous solutions by complexing with S-hydroxyethylglycine and extracting into methylisobutylketone (MIBK). The MIBK extract is then read for aluminum on the atomic absorption spectrophotometer using a nitrous oxide flame.

**KEYWORDS**
- Aluminum
- Glycol
- Atomic absorption
- Corrosion
- Testing
- Houston Chemical Company
- Solar cells
- Hydrochloric acid
- Nitric acid
- Ammonium hydroxide
- Ammonium acetate
- Glacial acetic acid
- Aluminum, 1000 ppm standard solution: Dissolve 1.000 g of aluminum wire or foil in a minimum amount of 1:1 HCl, add 1 drop of mercury as a catalyst, cool in a water bath to prevent aluminum oxide formation. Dissolve 1.000 g of aluminum wire or foil in a minimum amount of 1:1 HCl, add 1 drop of mercury as a catalyst, cool in a water bath to prevent aluminum oxide formation.

**SOLUTIONS AND REAGENTS**

Volumetric flasks, 200-ml.

Ammonium hydroxide, reagent grade.

Ammonium acetate, reagent grade.

Nitric acid, 1:1, prepare with analytical reagent HNO3.

Hydrochloric acid, 1:1, prepare with analytical reagent HCl.

Hydrochloric acid, 1:1, prepare with analytical reagent HCl.

(Vol solutions are prepared with double distilled water.)

**EQUIPMENT**

Solar cells

Houston Chemical Company

Television

Corrosion

Atometric absorption

Flame

Aluminum

**SUMMARY**

March 4, 1977

**APPENDIX 1**
addition preparation immediately following each other.

PROCEDURE

No./:

Clean all glassware immediately before use with warm LI. niter acetone and

PROCEDURE

1. Pipet a volume of sample containing from 20 to 50 ug Al (less than 75 ml) of concentrated nitric acid added and transfer each to 3 separate 150-ml graduated beakers.

I. Place a volume of sample containing from 20 to 70 ml of the blank, less than 75 ml, of concentrated nitric acid added and transfer to 3 beakers.

PROCEDURE

Note: Clean all glassware immediately before use with warm LI. niter acetone and

PROCEDURE

7. Add 2.0 ml of 8-hydroxyquinoline to each flask from Step 2. Shake vigorously for 15 seconds. NOTE: This step must be carried out without interruption for each

PROCEDURE

2. Adjust the solution volumes from Step 1 to 100 ml using deionized water.

PROCEDURE

Note: Clean all glassware immediately before use with warm LI. niter acetone and

PROCEDURE

4. Allow the layers to separate and add sufficient deionized water to bring the

PROCEDURE

5. Read in triplicate each sample, water blank, and sample plus standard

PROCEDURE

6. Read in triplicate each sample, water blank, and sample plus standard

PROCEDURE

3. Add 2.0 ml of 8-hydroxyquinoline to each flask from Step 2. Shake vigorously for 15 seconds. NOTE: This step must be carried out without interruption for each

PROCEDURE

1. Pipet a volume of sample containing from 20 to 50 ug Al (less than 75 ml) of concentrated nitric acid added and transfer each to 3 separate 150-ml graduated beakers.

I. Place a volume of sample containing from 20 to 70 ml of the blank, less than 75 ml, of concentrated nitric acid added and transfer to 3 beakers.

PROCEDURE

Note: Clean all glassware immediately before use with warm LI. niter acetone and

PROCEDURE

7. Add 2.0 ml of 8-hydroxyquinoline to each flask from Step 2. Shake vigorously for 15 seconds. NOTE: This step must be carried out without interruption for each

PROCEDURE
Flame Type: Nitrous oxide-acetylene adjusted to a rose-red inner cone, 1/2 to 3/4 -inch high. The outer flame will be 12 to 14 inches high.

Filter: Off.

Signal: In, grate 2.

**CALCULATION**

1. Average all absorbance readings.

2. Determine the net sample absorbance, \( A_s \), by subtracting the average blank absorbance, \( A_b \), from the average sample absorbance, \( A_{sample} \).

3. Determine a calibration factor, \( F \), for each sample using the relationship:

\[
F = \frac{A_{sample}}{A_{blank}}
\]

4. Determine the concentration of aluminum in the sample using the relationship:

\[
\text{Al, mg/l} = \frac{A_{sample} \times F}{mL \times \text{sample size}}
\]

Where:
- \( A_{sample} \) = average absorbance of the sample
- \( F \) = calibration factor for each sample
- \( mL \times \text{sample size} \) = that sample size under PROCEDURE.

If \( A_{sample} \) is greater than the denominator in Step 3, the determination should be repeated with a smaller sample size.

**ACCURACY AND PRECISION**

Recoveries of standard additions of 20 mg of Al to a sample of Propylene Glycol formulation and two Ethylene Glycol formulations were 94, 110, and 96\%, respectively, indicating acceptable results. Recoveries of standard additions of 20 mg of Al to a sample of Propylene Glycol formulation added at 20 mg were 94, 110, and 96\%, respectively, indicating acceptable results.

**DISCUSSION**

The sensitivity factor, \( F \), varies significantly from sample to sample and should, therefore, be determined for each sample. The sensitivity factor, \( F \), varies significantly from sample to sample and should, therefore, be determined for each sample.

**REFERENCES**


Charles L. Holifield
Research Chemist
Determination of copper, iron, and lead in crystal solutions.

**Summary**

As little as 0.02 mg/l Cu and 0.06 mg/l Fe or Pb may be determined by adjusting the pH of aqueous elual solutions to 1.6 and extracting the respective cations as their diethyl dithiocarbamate (DDC) complexes into a methyl isobutyl ketone (MIBK) phase. Following extraction, the organic phase is analyzed for the respective elements by atomic absorption (AA).

<table>
<thead>
<tr>
<th>KEYWORDS</th>
<th>EQUIPMENT</th>
<th>SOLUTIONS AND REAGENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Atomic absorption spectrometer, Perkin-Elmer Model 306, or equivalent, with an air/acetylene burner and Cu, Fe and Pb hollow cathode tubes.</td>
<td>Methyl isobutyl ketone, MIBK, analytical reagent saturated with deionized water.</td>
</tr>
<tr>
<td>Iron</td>
<td>pH meter.</td>
<td>Hydrochloric acid, HCl, 1 M. Carefully dilute 9.6 g (48 ml) of concentrated HCl to 100 ml with deionized water.</td>
</tr>
<tr>
<td>Lead</td>
<td>Millipore filtering apparatus, 25-mm diameter filter with 0.45-μm pore diameter, or separatory funnel, 150- and 250-ml with Teflon stopcocks.</td>
<td>Hydrochloric acid, HCl, concentrated analytical reagent.</td>
</tr>
<tr>
<td>Corrosion</td>
<td>Analytical methods</td>
<td>Sodium hydroxide, NaOH, 1 M. Carefully dissolve 4 g of analytical reagent NaOH and dilute to 100 ml with deionized water.</td>
</tr>
</tbody>
</table>

**Methods**

February 20, 1977
Diethyl dithiocarbamate sodium salt in 190 ml lore filter. Extract the solutions from Step 2 above to 3 separate 150-ml beakers, from 5 to 50 ml of each, and add 2 ml of 1 M nitric acid to 100 ml. Adjust the pH of each to 3.6 ± 0.1. Add 15 ml of DDG solution, 15 ml of KI, and 5 ml of concentrated HNO₃ plus 2.0 ml of each of the working standards of Cu, Fe, and Pb. Adjust each solution (blank) from 5 to 50 ml of sample, and sample (the same volume as selected above) to 100 ml with deionized water. Then add all glassware with 1:1 HNO₃ and then deionized water.

**Procedure**

1. Deliver into 3 separate 150-ml beakers from 5 to 50 ml of deionized water (blank), from 5 to 50 ml of sample, and sample (the same volume as selected above) plus 1.00-ml each of the working standards of Cu, Fe, and Pb. Adjust each solution to 100 ml with deionized water.

2. Dilute to 1.000 liter with deionized water.

3. Acidify the solutions from Step 1 with concentrated HNO₃, add 2 ml of phthalate buffer and adjust the pH to 3.6 ± 0.1. Add 7 ml DDG solution, 15 ml of KI, and 2 ml of concentrated HNO₃ and allow the phases to separate and draw off the KI/phase into a 150-ml beaker.

4. Transfer the solutions from Step 2 above to 3 separate 150-ml beakers, from 5 to 50 ml of each, and add 2 ml of 1 M nitric acid to 100 ml. Adjust the pH of each to 3.6 ± 0.1. Add 15 ml of DDG solution, 15 ml of KI, and 5 ml of concentrated HNO₃ plus 2.0 ml of each of the working standards of Cu, Fe, and Pb. Adjust each solution (blank) from 5 to 50 ml of sample, and sample (the same volume as selected above) to 100 ml with deionized water. Then add all glassware with 1:1 HNO₃ and then deionized water.

**NOTE:** Immediately before use, transfer all glassware with 1:1 HNO₃ and then deionized water.

Lead, working standard, 100 mg/l Pb: Dissolve 1.00 g Pb(NO₃)₂ in 1% H₂SO₄, dilute to 1.000 liter with 1% HNO₃.

Lead, working standard, 5.0 mg/l Pb: Dilute 10.00 ml of 1.00 g/l lead standard to 100.0 ml using deionized water.

Copper, standard solution, 1.00 g/l Cu: Dissolve 1.00 g copper metal in a Mini-mula volume of 1:1 HNO₃, dilute to 1.000 liter with 1:1 HNO₃.

Copper, working standard, 10.0 mg/l Cu: Dilute 1.00 g/l Cu standard solution 10.00 ml to 100.0 ml, out 25.0 ml to 200.0 ml. Prepare fresh daily.

Iron, standard solution 1.00 g/l Fe: Dissolve 1.00 g iron wire in 50 ml of 1:1 HNO₃. Dilute to 1.000 liter with deionized water.

Iron, working standard, 50 mg/l Fe: Dilute 1.00 g/l Fe standard solution 10.00 ml to 100.0 ml, out 25.0 ml to 100.0 ml using deionized water.

Lead, standard solution, 1.00 g/l Pb: Dissolve 1.00 g Pb(NO₃)₂ in 1% H₂SO₄, dilute to 1.000 liter with 1% HNO₃.

Lead, working standard, 25 mg/l Pb: Dilute 10.00 ml of 1.00 g/l lead standard to 100.0 ml using deionized water.

PROCEDURE

Immediately before use, transfer all glassware with 1:1 HNO₃ and then deionized water.

1. Deliver into 3 separate 150-ml beakers from 5 to 50 ml of deionized water (blank), from 5 to 50 ml of sample, and sample (the same volume as selected above) plus 1.00-ml each of the working standards of Cu, Fe, and Pb. Adjust each solution to 100 ml with deionized water.

2. Dilute to 1.000 liter with deionized water.

3. Acidify the solutions from Step 1 with concentrated HNO₃, add 2 ml of phthalate buffer and adjust the pH to 3.6 ± 0.1. Add 7 ml DDG solution, 15 ml of KI, and 2 ml of concentrated HNO₃ and allow the phases to separate and draw off the KI/phase into a 150-ml beaker.

4. Transfer the solutions from Step 2 above to 3 separate 150-ml beakers, from 5 to 50 ml of each, and add 2 ml of 1 M nitric acid to 100 ml. Adjust the pH of each to 3.6 ± 0.1. Add 15 ml of DDG solution, 15 ml of KI, and 5 ml of concentrated HNO₃ plus 2.0 ml of each of the working standards of Cu, Fe, and Pb. Adjust each solution (blank) from 5 to 50 ml of sample, and sample (the same volume as selected above) to 100 ml with deionized water. Then add all glassware with 1:1 HNO₃ and then deionized water.

5. Acidify the solutions from Step 1 with concentrated HNO₃, add 2 ml of phthalate buffer and adjust the pH to 3.6 ± 0.1. Add 7 ml DDG solution, 15 ml of KI, and 2 ml of concentrated HNO₃ and allow the phases to separate and draw off the KI/phase into a 150-ml beaker.

6. Transfer the solutions from Step 2 above to 3 separate 150-ml beakers, from 5 to 50 ml of each, and add 2 ml of 1 M nitric acid to 100 ml. Adjust the pH of each to 3.6 ± 0.1. Add 15 ml of DDG solution, 15 ml of KI, and 5 ml of concentrated HNO₃ plus 2.0 ml of each of the working standards of Cu, Fe, and Pb. Adjust each solution (blank) from 5 to 50 ml of sample, and sample (the same volume as selected above) to 100 ml with deionized water. Then add all glassware with 1:1 HNO₃ and then deionized water.

7. Acidify the solutions from Step 1 with concentrated HNO₃, add 2 ml of phthalate buffer and adjust the pH to 3.6 ± 0.1. Add 7 ml DDG solution, 15 ml of KI, and 2 ml of concentrated HNO₃ and allow the phases to separate and draw off the KI/phase into a 150-ml beaker.
A. For Copper:

Cu Hollow Cathode Lamp, Wavelength: 325 nm (set for maximum energy at approximately 325 using the UV scale).

Air Pressure: 12 psig;
Acetylene Pressure: 30 psig;
Mode: Absorbance;
Source: Absorbance;
Gain: As required to bring energy meter in working range;
Aspiration Rate: 5.0–5.5 ml/minute for MSK;
Filter: Off;
Signal: Integrate 2.

NOTE: Read the absorbance of each sample using the same conditions.

B. For Iron:

Fe Hollow Cathode Lamp, Wavelength: 248.3 nm (set for maximum energy at approximately 248 using the UV scale).

Air Pressure: 12 psig;
Acetylene Pressure: 30 psig;
Mode: Absorbance;
Source: Absorbance;
Gain: As required to bring energy meter in working range;
Aspiration Rate: 5.0–5.5 ml/minute for MSK;
Filter: Off;
Signal: Integrate 2.

NOTE: See instruction under Copper conditions concerning MSK/water aspiration.

C. For Lead:

Pb Hollow Cathode Lamp, Wavelength: 283.3 nm (set for maximum energy at approximately 283 using the UV scale).

Air Pressure: 12 psig;
Acetylene Pressure: 30 psig;
Mode: Absorbance;
Source: Absorbance;
Gain: As required to bring energy meter in working range;
Aspiration Rate: 5.0–5.5 ml/minute for MSK;
Filter: Off;
Signal: Integrate 2.

NOTE: See instruction under Copper conditions concerning MSK/water aspiration.
The efficiency of extraction of copper, iron and lead is dramatically reduced by the glycol content in the aqueous phase during the extraction. Consequently, the recovery of standard additions to typical glycol samples are summarized in Table I.

### Table I

<table>
<thead>
<tr>
<th>Sample</th>
<th>Recovery of Standard Additions of Cu, Fe and Pb to Glycol Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**ACCURACY AND PRECISION**

Recoveries of standard additions to typical glycol samples are summarized in Table I.

**NOTE**

*See instruction under copper conditions concerning HIBK/water application.*

**Fluor**

*Off*

**Stir**

*Integra 2*

**Absorption Rate**

5.0-5.5 ml/minute for HIBK.
important that a calibration factor, F, be established for each sample size taken; i.e., the same volume of unknown must be taken for both the sample and the sample plus standard addition and carried through the procedure.

REFERENCES

Perkin-Elmer Analytical Method EN-8, September, 1976.