AEC RESEARCH AND DEVELOPMENT REPORT

642
Y-1661
Chemistry

MASTER

214
2-7-69

DETERMINATION OF TRACE ZINC IN LITHIUM
COMPOUNDS BY ATOMIC ABSORPTION
SPECTROPHOTOMETRY

R. E. Barringer
H. G. King
A. D. Condrey

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the ATOMIC ENERGY COMMISSION under U. S. GOVERNMENT Contract W-7405 eng 26

**UNION
CARBIDE**

OAK RIDGE Y-12 PLANT
P. O. Box Y
OAK RIDGE, TENNESSEE 37830

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U.S. Department of Commerce, Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Date Issued: February 3, 1969

Document Y-1661

Chemistry
TID-4500

UNION CARBIDE CORPORATION
Nuclear Division

Y-12 PLANT

Contract W-7405-eng-26
With the US Atomic Energy Commission

DETERMINATION OF TRACE ZINC IN LITHIUM COMPOUNDS
BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

R. E. Barringer
H. G. King
A. D. Condrey

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Oak Ridge, Tennessee

leg

Document Y-1661Chemistry
TID-4500

Distribution:

Ballenger, H. F. (2)
Barringer, R. E. (5)
Bell, B. B.
Bernander, N. K.
Briscoe, O. W.
Burkhart, L. E.
Clark, F. E.
Condrey, A. D. (5)
Dill, M. S.
Evans, G. W.
Freels, W. A.
Hemphill, L. F.
Horde, G. W. (2)
Jordan, R. G. (ORGDP)
Kahl, K. G.
Keith, Alvin (2)
Keller, C. A. (AEC-ORO)
King, H. G. (5)
McLendon, J. D.
Meeks, E. J. (AFSC)
Mitchel, G. W.
Phillips, L. R.
Rowan, J. H.
Vanstrum, P. R. (ORGDP)
Wesley, R. L.
Winkel, R. A. (Paducah)
Yaggi, W. J.
Y-12 Central Files (5)
Y-12 Central Files (Route)
Y-12 Central Files (Y-12RC)

In addition, this report is distributed in accordance with the category Chemistry, as given in the "USAEC Standard Distribution Lists for Unclassified Scientific and Technical Progress Reports", TID-4500.

ABSTRACT

Two procedures were developed for the analysis of zinc in lithium compounds by atomic absorption spectrophotometry: (1) a direct method of aspirating a lithium solution into the burner of an atomic absorption spectrophotometer gave a sensitivity to four micrograms zinc per gram of lithium; (2) a method in which zinc was extracted into 2-heptanone before aspiration could be extended readily to a sensitivity of 0.1 microgram zinc per gram of lithium.

CONTENTS

SUMMARY	5
INTRODUCTION	6
DIRECT ASPIRATION METHOD	7
General Procedure	7
Reagents and Equipment	7
Reagents.	7
Standard Solutions	7
Special Equipment	8
Calibration Method.	8
Sample Preparation	9
Sample Analysis	9
Discussion.	10
EXTRACTION METHOD	12
General Procedure	12
Reagents and Equipment	12
Reagents.	12
Standard Solutions	12
Special Equipment	13
Calibration Method.	13
Sample Analysis	15
Discussion.	15
History and Advantages of Extraction	15
Parameters Affecting Extraction	16
Special Techniques	17
Parameters Affecting Absorption Readings.	18
Calibration and Sample Results	19
Applicability of the Method	21
REFERENCES	23

SUMMARY

Atomic absorption spectrophotometric techniques have been applied to the analysis of trace quantities of zinc in lithium compounds. A method of directly aspirating the sample solution into the air-acetylene flame provided simplicity of sample preparation and required a minimum amount of time. A sensitivity of four micrograms zinc per gram of lithium was generally achieved for most samples. The limit of error (0.95) of a single direct measurement was ± 1 microgram zinc per gram lithium over the concentration range of 10 to 200 micrograms.

In a second method of analysis, the zinc was separated from the lithium matrix by extraction as a complex with ammonium pyrrolidine dithiocarbamate into 2-heptanone. Good extraction was obtained from solutions adjusted to a pH of 3.0 - 5.5. This technique resulted in increased sensitivity to 0.1 microgram zinc per gram lithium and provided virtual freedom from burner clogging in the aspiration step. The limit of error (0.95) for a single determination varied from ± 0.7 microgram zinc per gram of sample, for a concentration of three micrograms zinc per gram of sample, to ± 3 micrograms zinc per gram of sample, for a concentration of 30 micrograms zinc per gram of sample.

INTRODUCTION

Existing methods for determining trace amounts of zinc in lithium compounds all have some deficiency. Emission-spectrographic methods are relatively limited in sensitivity; difficulties in instrument control under routine conditions attach undesirable features to an otherwise suitable polarographic method;⁽¹⁾ colorimetric methods are generally tedious and suffer from interference by impurities which may be present.

Atomic absorption techniques offered a way which held promise of adequate sensitivity and selectivity plus a simplicity of operation which is practical for routine usage.

DIRECT ASPIRATION METHOD

GENERAL PROCEDURE

A direct aspiration procedure was developed for the determination of zinc in lithium compounds. The sample is dissolved and the resulting solution aspirated directly into the burner of an atomic absorption spectrophotometer. This method requires a very simple preparation procedure and a minimum of time and effort to complete the analysis.

REAGENTS AND EQUIPMENT

Reagents

Zinc Metal - High purity.

Hydrochloric Acid - Reagent grade (check for low zinc content).

Nitric Acid - Reagent grade (check for low zinc content).

Lithium Carbonate - ARL, high purity (zinc free).

Distilled Water - Zinc free (demonstrated zinc concentration < 0.01 ppm).

Standard Solutions

Stock Zinc Solution (1,000 μg s Zn/ml) - Dissolve 1.000 gram of mossy zinc in 100 mls of 1:3 hydrochloric acid. Cool and dilute to one liter with water.

Standard Zinc Solution (5 μg s Zn/ml) - Dilute 5 mls of the 1,000 μg s Zn/ml stock solution plus 10 mls of concentrated hydrochloric acid to one liter with distilled water.

Standard Zinc-in-Lithium Solutions - To make solutions having 2,500 micrograms of lithium per milliliter of solution, containing the equivalent of 0, 10, 20, 40, 80, and 200 micrograms of zinc per gram of lithium, add to each of six 100-ml volumetric flasks 1.33 grams of lithium carbonate dissolved in hydrochloric acid and 0, 0.5, 1, 2, 4, and 10 mls of the standard zinc solution. Dilute to volume with water and mix well. Concentrations are equal to 0, 2.5, 5, 10, 20, and 50 μg s of zinc in the 100-ml flasks.

Special Equipment

Atomic Absorption Spectrophotometer, Perkin-Elmer Model 303 - Consists of the spectrophotometer with an air-acetylene burner atomizer assembly, burner regulator, zinc hollow cathode lamp, and null meter readout.

CALIBRATION METHOD

The spectrophotometer should be calibrated according to the following procedure:

1. Set the instrument to the parameters listed in Table 1 and allow a 20-minute warmup period.

Table 1
SPECTROPHOTOMETER OPERATING PARAMETERS
(Zinc in Lithium by the Direct Method)

Lamp Type	Zinc, Hollow Cathode
Source Current	10 ma
Slit Width	5 (3 mm)
Range	UV
Wavelength	2138 Å
Fuel Pressure (acetylene)	8 psi
Fuel Flow	9.0 on the Flowmeter
Air Pressure	20 - 30 psi
Air Flow	9.0 on the Flowmeter
Sample Uptake Rate	4 ml/min (H ₂ O)

2. Ignite the flame.
3. Aspirate the blank lithium solution (0 µg Zn/gm Li) into the burner. Allow the aspiration to continue to obtain a stable reading. After about 30 seconds, adjust the percent absorption meter to read zero.
4. Aspirate distilled water between each solution to thoroughly flush the burner.
5. Aspirate each standard zinc solution (10 to 200 µg Zn/gm Li) into the burner in random order. After a stable reading is reached, null the meter and read the percent absorption. Repeat in different order for a second reading on each standard solution.
6. Convert the percent absorption readings to absorbance using the table provided by the manufacturer. A plot of concentration (µg Zn/gm Li) versus absorbance should be linear.
7. Calculate a calibration factor in terms of absorbance per microgram zinc per gram lithium as follows:

$$\text{Factor A} = \frac{\frac{\text{Absorbance of Std A}}{\mu\text{gs Zn/gm Li in Std A}} + \frac{\text{Absorbance of Std B}}{\mu\text{gs Zn/gm Li in Std B}} + \frac{\text{Absorbance of Std N}}{\mu\text{gs Zn/gm Li in Std N}}}{N},$$

or a factor in terms of absorbance per microgram zinc in a 100-ml flask:

$$\text{Factor B} = \frac{\frac{\text{Absorbance of Std A}}{\mu\text{gs Zn in Flask A}} + \frac{\text{Absorbance of Std B}}{\mu\text{gs Zn in Flask B}} + \frac{\text{Absorbance of Std N}}{\mu\text{gs Zn in Flask N}}}{N},$$

when N is the number of standards measured.

SAMPLE PREPARATION

Prepare a hydrochloric acid solution containing 0.250 gram lithium in a 100-ml volume. Lithium salts, hydroxide, or carbonate are dissolved in a 1:1 hydrochloric acid solution, diluted with water to volume in a 100-ml volumetric flask, and mixed thoroughly. From liquid samples, an aliquot containing 0.250 gram lithium is acidified and diluted to volume in a 100-ml volumetric flask. If the exact lithium content of the sample is unknown, use a weighed amount of sample approximating 0.250 gram of lithium.

SAMPLE ANALYSIS

Analysis of a sample can be accomplished as follows:

1. Set the atomic absorption spectrophotometer to the parameters listed in Table 1 and allow for a 20-minute warmup period.
2. Ignite the flame.
3. Aspirate the blank lithium solution (0 $\mu\text{g Zn/gm Li}$) into the burner. Allow the aspiration to continue about 30 seconds to obtain a stable reading. Adjust the percent absorption meter to read zero.
4. Aspirate distilled water between each solution to thoroughly flush the burner.
5. Aspirate the sample solution into the burner. After a stable reading is reached, null the meter and read the percent absorption.
6. Convert the percent absorption readings to absorbance using a table provided by the manufacturer.

7. Calculate the concentration of zinc in the original sample using the previously determined calibration factors.

$$\text{Zinc Concentration } (\mu\text{gs Zn/gm Li}) = \frac{\text{Absorbance of Sample}}{\text{Factor A}}, \text{ or}$$

$$\text{Zinc Concentration } (\mu\text{gs Zn/gm sample}) = \frac{\text{Absorbance of Sample}}{\text{Factor B} \times \text{Sample Weight (gms)}}.$$

DISCUSSION

Standard zinc solutions were prepared both in aqueous media and in lithium solutions containing 2,500 micrograms of lithium per milliliter. Figure 1 shows a plot of the zinc concentration versus absorbance from both sets of standards. Aspirations of similar zinc concentrations in the presence or absence of lithium gave similar absorbances, indicating that the sample beam scattering by salt particles in the flame was negligible. A linear response was obtained for zinc concentrations from 10 to 200 micrograms zinc per gram of lithium. The method could be successfully applied for the determination of as little as four micrograms of zinc per gram of lithium in solutions containing 2,500 micrograms of lithium per milliliter.

The analysis of five solutions of lithium concentration variant from 500 to 12,500 micrograms per milliliter produced nearly equal absorbance values. Slightly greater absorbances at the greater lithium concentrations indicated that the lithium-based

Figure 1. CALIBRATION OF ZINC IN LITHIUM BY THE DIRECT ASPIRATION METHOD.

materials contained a small amount of residual zinc. Burner clogging was experienced with solutions containing more than 2,500 micrograms of lithium per milliliter. Extended operations at the greater lithium concentrations would, therefore, be undesirable.

The atomizer and burner were cleaned by aspirating a 1:4 nitric acid solution followed by a water flush. Flushing thoroughly with water between each sample solution retarded the buildup of cake in the burner. When it became necessary to remove caked material from the burner slot, a fast cut-off valve in the fuel line was closed and a razor blade or other thin metal piece was passed along the slot while the burner air was still flowing. The fuel valve was then reopened and the flame quickly reignited.

Two samples were each spiked with zinc at the two and four-microgram zinc per milliliter level. Analysis of the spiked solutions showed satisfactory recovery of the spikes, as the data of Table 2 indicate.

Table 2
ZINC RECOVERY IN SPIKED SALT SOLUTIONS

Sample Number	Zinc Added ($\mu\text{g}/\text{ml}$)	Zinc Recovered ($\mu\text{g}/\text{ml}$)
1	4.0	3.8
2	2.0	2.0
3	4.0	3.6
4	2.0	2.1

To determine the precision of measurement, two sets of standard solutions (consisting of five standards each at concentration levels of 0.025 to 0.5 microgram zinc per milliliter) were aspirated and absorbance measured twice daily for four days. Over this range (equivalent to 10 to 200 micrograms zinc per gram lithium) statistical evaluation of the data revealed a limit of error (0.95) of a single measurement of absorbance of ± 1 microgram zinc per gram lithium, as reported in Table 3.

Table 3
PRECISION OF THE DETERMINATION OF TRACE ZINC IN LITHIUM

Standard Number	Concentration		$LE_x (0.95)$ ($\pm \mu\text{g Zn/gm Li}$)
	$\mu\text{g Zn/gm Li}$	$\mu\text{g Zn/ml Solution}$	
1	10	0.025	1.1
2	20	0.050	1.2
3	40	0.100	1.3
4	80	0.200	1.1
5	200	0.500	1.2

Other topics applicable to both methods of analysis are discussed under the extraction procedure (Page 15).

EXTRACTION METHOD

GENERAL PROCEDURE

An extraction procedure was developed to overcome some of the difficulties encountered with the direct procedure. The lithium-containing sample was dissolved and the resulting solution extracted. Ammonium pyrrolidine dithiocarbamate (APDTC) served as the complexing agent for the zinc which was extracted under controlled pH conditions into 2-heptanone. A final absorption measurement was obtained by aspirating the 2-heptanone extract directly into the burner of the atomic absorption spectrophotometer.

REAGENTS AND EQUIPMENT

Reagents

Ammonium Pyrrolidine Dithiocarbamate (APDTC), 1% - Solution made by dissolving 1.000 gram of the reagent in approximately 50 mls of water. The mixture was then filtered through Whatman 41 paper and made to a final volume of 100 mls with water.

2-Heptanone (methyl n-amyl ketone) - Solution filtered through Whatman 42 paper.

Mossy Zinc - High purity.

Hydrochloric Acid - Reagent grade (check for low zinc content).

Hydrochloric Acid - Diluted 4 mls to 100 mls with water.

Ammonium Hydroxide - Reagent grade (check for low zinc content).

Ammonium Hydroxide - Diluted 4 mls to 100 mls with water.

Tetrabromophenolsulfonephthalein (bromophenol blue), 0.1% W/V - Made by dissolving 0.1 gram of reagent in 100 mls of 20% ethanol solution.

Distilled Water - Zinc free.

Standard Solutions

Stock Zinc Solution (1,000 μ gs Zn/ml) - Dissolve 1.000 gram of mossy zinc in 100 mls of a 25% hydrochloric acid solution. Cool and dilute the mixture to one liter with water.

Standard Zinc Solution (25 $\mu\text{gs Zn/ml}$) - Dilute 5 mls of the 1,000 $\mu\text{gs Zn/ml}$ stock solution plus 10 mls of concentrated hydrochloric acid to 200 mls with water.

Standard Zinc Solution (2.5 $\mu\text{gs Zn/ml}$) - Dilute 25 mls of the 25 $\mu\text{gs Zn/ml}$ standard solution to 250 mls with water.

Special Equipment

Atomic Absorption Spectrophotometer, Perkin-Elmer Model 303 - Consists of the spectrophotometer with an air-acetylene burner atomizer assembly, burner regulator, zinc hollow cathode source lamp, recorder readout, and 10-millivolt strip chart recorder. The recorder was equipped with paper evenly graduated (100-0-10 divisions).

Separatory Funnels - Volume of 125 mls and with Teflon stopcocks.

Dropper Bottles - All plastic - no rubber bulbs.

CALIBRATION METHOD

The spectrophotometer should be calibrated according to the following procedure:

1. Prepare duplicate calibration standards at each concentration level by pipetting into 125-ml separatory funnels, 0, 1, 2, 3, 4, and 5 mls of the 2.5 $\mu\text{gs Zn/ml}$ standard solution representing 0 to 1.25 $\mu\text{gs Zn/ml}$ of 2-heptanone extract.
2. Dilute to approximately 25 mls with distilled water.
3. Add 2 drops of 0.1 percent bromophenol blue.
4. Add 1.5 mls of 1 percent APDIC.
5. Adjust the pH of the aqueous solution to between 3.0 and 5.0 by the dropwise addition of dilute ammonium hydroxide or hydrochloric acid to a faint blue color.
6. Add 10 mls of 2-heptanone.
7. Shake the mixture for one minute, then after the layers have separated for approximately 15 minutes, drain off and discard the aqueous layers leaving the organic layers in the separatory funnels.
8. Set the atomic absorption spectrophotometer to the parameters for zinc given in Table 4 and allow for a 20-minute warmup period.

Table 4
SPECTROPHOTOMETER OPERATING PARAMETERS
(Zinc in Lithium by the Extraction Method)

Lamp Type	Zinc, Hollow Cathode
Source Current	10 ma
Slit Width	5 (3 mm)
Range	UV
Wavelength	2138 Å
Fuel Pressure (acetylene)	8 psi
Fuel Flow	9.0 on the Flowmeter
Air Pressure	20 - 30 psi
Air Flow	9.0 on the Flowmeter
Sample Uptake Rate	4 ml/min (H ₂ O)
Noise Suppression	3
Scale Expansion	X1
Recorder Sensitivity	10 mv

9. Ignite the flame.
10. Aspirate new 2-heptanone into the burner, set the recorder pen near zero with the "full-scale" control, and continue aspirating the 2-heptanone until the recorder trace ceases to drift.
11. Aspirate the 2-heptanone extract of the blank directly from the separatory funnel and set the recorder pen to zero. Once the zero has been set, instrument drift can be checked and the zero reset by referring to the new 2-heptanone reading.
12. Aspirate each of the remaining 2-heptanone extracts of standards until the zinc peak on the recorder chart has reached its maximum.
13. Aspirate the blank new 2-heptanone between each sample to flush the burner and to occasionally recheck the zero.
14. From the recorder chart, read the percent zinc absorption to the nearest half division for each standard.
15. Average the absorption readings for each standard and convert the results to absorbance. A plot of concentrations ($\mu\text{g Zn/ml 2-heptanone}$) versus absorbance should be linear.
16. Calculate a factor from the standards data using the expression:

$$\text{Factor} = \frac{\sum \text{Concentration } (\mu\text{g Zn/ml 2-heptanone})}{\sum \text{Absorbance}} .$$

SAMPLE ANALYSIS

Analysis of a sample can be accomplished as follows:

1. Pipette duplicate 25-ml aliquots of each sample solution into 125-ml separatory funnels. A blank is analyzed using approximately 25 mls of zinc-free water with concentrated hydrochloric acid added in quantities needed as indicated in Step 4.
2. Add 2 drops of 0.1 percent bromophenol blue.
3. Add 1.5 mls of 1 percent APDTC.
4. Adjust the pH of the aqueous solution between values of 3.0 and 5.0 by the dropwise addition of concentrated hydrochloric acid to the endpoint as indicated by the color change. Final adjustment is made by adding dilute ammonium hydroxide or hydrochloric acid until a faint blue color is obtained.
5. Add 5 mls of 2-heptanone.
6. Follow the proposed calibration procedure (Steps 7 - 14) to obtain absorption readings for each sample.
7. Average the absorption readings for each sample and convert the results to absorbance. Using the factor from the calibration curve, determine the concentration of each sample from the equation:

$$\text{Zinc Concentration} = \frac{\text{Factor} \times \text{Absorbance} \times \text{mls Heptanone} \times \text{Dilution Factor}}{\text{Sample Weight}}$$

DISCUSSION

History and Advantages of Extraction

Allan⁽²⁾ used an organic solvent extraction of zinc from agricultural materials employing ammonium pyrrolidine dithiocarbamate as a complexing agent. Willis⁽³⁾ employed the same complexing agent to extract heavy metals from urine into methyl-n-amyl-ketone (2-heptanone) followed by atomic absorption analysis. Allan⁽⁴⁾ studied the choice of solvents most suitable for spraying into atomic absorption flames.

Some of the advantages of extraction are: (1) it provides the possibility of analyzing more concentrated lithium sample solutions than the direct method permitted;

(2) almost complete elimination of burner clogging is attained; (3) increased sensitivity in the flame from the use of solvent medium is realized; (4) obtaining concentration factors is possible by the use of high sample-to-solvent extraction ratios.

Parameters Affecting Extraction

In this present study various parameters affecting the extraction of zinc were investigated.

Extraction - Zinc was extracted reproducibly using extraction ratios up to one volume of 2-heptanone to ten volumes of the sample solution. At this 1 to 10 ratio it was found most important to achieve good intermixing of the phases. Separatory funnels filled more than at two-thirds capacity did not undergo the necessary mixing action by a normal one-minute shaking time to yield consistent results.

Range of pH Values - A solution pH range of 3.0 to 5.5 before adding 2-heptanone for extraction proved suitable for complete extraction. At a pH value of 2.5, decreased zinc recovery was noted. Adequate control of pH was achieved by the use of bromophenol blue indicator, a method that was simpler and less subject to trace contamination than employing a pH meter.

Extraction Medium - As reported by Allan, (2) it was confirmed that nitric or hydrochloric acid served equally well for an extraction medium. Hydrochloric acid was chosen because of a preference in handling, the effects being less vigorous than those of nitric acid should the strong acids come in contact with the hands or person. Also, nitric acid solutions standing for periods of time in contact with organic materials can result in vigorous reactions.

Complexing Agent - The extraction of zinc by 2-heptanone in the presence of ammonium pyrrolidine dithiocarbamate was found to be equally effective from water solution or from solutions containing as much as 4 grams of lithium per 100 milliliters of solution as the lithium chloride (~ 1/4 saturated).

Experiments have shown that three milliliters of one percent ammonium pyrrolidine dithiocarbamate (APDTC) is more than adequate to complex 1,000 micrograms of zinc. With relatively pure lithium compounds, adequate excess of complexing agent is available to complex any other trace metals that might be present. Malissa and Schoffmann(5) report other elements complexed by APDTC are: antimony, arsenic, bismuth, cadmium, chromium, cobalt, copper, gold, iridium, iron, lead, manganese, mercury, molybdenum, nickel, niobium, osmium, palladium, platinum, rhodium, ruthenium, selenium, silver, tellurium, thallium, tin, tungsten, uranium, and vanadium.

If appreciable quantities of these elements are present as impurities, additional APDTC complexing agent may be necessary to insure complete extraction of the

zinc. Emission spectrographic analysis of typical lithium samples of interest in this work showed the total of the metallic impurities just listed to be less than 500 micrograms per gram. The quantity of ammonium pyrrolidine dithiocarbamate used in the extraction was more than sufficient to complex the impurities present.

Completeness of Extraction - Aqueous layers drawn off from the extraction of solutions containing 25 micrograms total zinc were extracted a second time. Additional complexing agent was added, the pH readjusted, and fresh 2-heptanone used. No zinc was found in the second solvent extract, indicating complete extraction of the zinc in the initial extraction. An additional extraction of aqueous layers from the extraction of solutions containing 250, 500, 750, and 1,000 micrograms total zinc showed recoveries of 0.2 to 1.3 micrograms of zinc. This insignificant percentage of the total zinc was believed to be present in the aqueous layers due to incomplete separation of tiny droplets of zinc-laden 2-heptanone in the initial extraction.

Various amounts of zinc were added to portions of a sample solution and the resulting solutions analyzed by the proposed extraction procedure. Recoveries were good, as shown in Table 5.

Table 5
ZINC RECOVERY FROM LITHIUM HYDROXIDE
SOLUTIONS BY AMMONIUM PYRROLIDINE
DITHIOCARBAMATE EXTRACTIONS

Zinc Added (μ gs)	Zinc Found (μ gs)	Zinc Recovered (μ gs)	Percent Recovery
0	0.58	-	-
1.25	1.81	1.23	98
2.50	3.07	2.49	100
5.00	5.29	4.71	94

Stability of the 2-Heptanone Extract - A stability study of the 2-heptanone extract of zinc showed a gradual decrease in absorption readings with time. After standing overnight, most of the zinc absorption was gone (Table 6). It was found that the zinc concentrated in the small amount of aqueous phase which settled out on the walls and in the tip of the separatory funnel used for extraction. From these studies it was concluded that absorption readings on the 2-heptanone extract should be taken as soon after extraction as practicable, but no more than two hours later for test results.

Special Techniques

In certain lithium chloride samples, finely divided solids settled out upon standing. Analyses for zinc by the extraction procedure yielded identical values for both the top layers which were clear and the bottom layers which were cloudy.

Table 6
STABILITY OF ZINC-2-HEPTANONE EXTRACT

Time After Extraction (hrs)	Instrument Reading (% absorption)		
	Blank	Sample Solution	Spiked Sample Solution
0.5	1.0	7.0	24.0
2.0	1.0	6.0	23.0
3.5	1.0	5.0	21.0
4.5	1.0	5.0	19.8
5.5	1.0	4.0	19.0
22.5	0.5	1.0	2.0

In common with all trace analysis methods, great care and cleanliness must be exercised to eliminate minor contamination. Among reagents it was found that nitric acid contained a trace less zinc than hydrochloric acid, although neither was significant. An aqueous solution of bromophenol blue indicator, prepared by first converting the indicator to salt by the addition of sodium hydroxide, showed small but erratic concentrations of zinc. Changing from an aqueous solution of the sodium salt to an alcoholic solution of the bromophenol blue indicator, eliminated most of the trace contamination arising from this source.

The acid, base, and indicator reagents were stored in all-plastic dropping bottles for dropwise addition as needed. Storage in dropping bottles, equipped with rubber bulbs on medicine droppers for dispensing solutions, produced eventual contamination of reagents from the rubber even though the solution was never drawn into the bulb.

Other unexpected sources of contamination can easily arise. For example, a few particles of face powder, acidified and extracted with ammonium pyrrolidine dithiocarbamate, resulted in a final instrument reading of 75 percent absorption. Thorough cleaning of the zinc-laden 2-heptanone from extraction flasks proved a very important step in this method. Some cleaning procedures proved much more effective than others. The use of a liquid detergent rinsed away the 2-heptanone much more effectively than did either an acetone or hydrochloric acid rinse. The laboratory water supply contained one microgram of zinc per milliliter. Therefore, the final rinse of the equipment was with distilled water. By using careful techniques, an extracted blank of reagents yielded only one percent absorption in the flame.

Parameters Affecting Absorption Readings

Lamp Warmup Time - Warmup time for the zinc hollow cathode lamp was found to require twenty minutes after the instrument was turned on. Thereafter, the lamp output remained relatively stable. Variation of the lamp current between 8 and 10 milliamperes showed a more reproducible absorption reading at the higher current.

Burner Operations - The burner was found to reach stable operating conditions after five minute's time. Variation of the fuel gas flow rate over a range of 8.5 to 9.5 setting on the flowmeter produced little effect on the net absorption. Flow rates of 9 to 9.5 on the flowmeter yielded almost identical absorption readings.

A small local exhaust hood over the burner, as recommended by the manufacturer, carried away vapors which would be injurious to the health of the operator or corrosive to the atomic absorption instrument.

Instrument Gain Control - Variation of the instrument gain control had no noticeable effect on the net absorption as long as the reference energy meter reading was within the prescribed operating range.

Recorder Equipment - Addition of a recorder readout accessory and strip-chart recorder provided greater certainty of readings with a shorter aspiration time, permitting readings to be taken with smaller volumes of solution. Repetitive measurements on the same solution were very reproducible and variations from solution to solution were shown to be due to factors other than absorption measurements.

Water Aspiration - The rate of water aspiration proved to be a very convenient check on the cleanliness of the aspirator. With the particular aspirator and oxygen flow used, the rate of aspiration was four milliliters per minute. A check made at each startup of the instrument quickly revealed any clogging of the aspirator.

Test Solution - As a check on instrument performance, a solution containing two micrograms of zinc per milliliter in dilute hydrochloric acid was aspirated into the flame. This solution gave a net reading of 36 percent absorption where zero was set against water. The water solution of zinc was selected because, as previously mentioned, zinc extracted into 2-heptanone did not retain its zinc concentration upon standing.

Calibration and Sample Results

Seven sets of zinc standards, providing concentrations ranging from 0.25 to 1.75 micrograms of zinc per milliliter of 2-heptanone extract, were each extracted and percent absorptions measured on seven different days. From the mean net absorbances obtained (Table 7), a plot of zinc concentration versus absorbance (Figure 2) was linear through 1.25 micrograms of zinc per milliliter of 2-heptanone extract.

A calibration factor of the form $\Sigma \text{Zn concentration} / \Sigma \text{absorbances}$ (Step 16 of the calibration, Page 14) covering this range was calculated. The calibration factor and its 95 percent confidence limit of error was 3.93 ± 0.05 micrograms of zinc

Table 7
CALIBRATION DATA FOR ZINC BY THE
EXTRACTION METHOD

Zinc Concentration (μg s Zn/ml 2-heptanone)	Mean Net Absorbance
0.25	0.0645
0.50	0.1308
0.75	0.1945
1.00	0.2541
1.25	0.3107
1.50	0.3565
1.75	0.4034

Figure 2. CALIBRATION FOR ZINC BY THE EXTRACTION METHOD.

per milliliter of 2-heptanone extract per absorbance unit. This form of calibration factor was chosen as a universal one, usable with varying quantities of the original lithium sample, varying concentrations of sample solutions, and with any chosen extraction ratio.

The lithium solutions were extracted in a 25-milliliter solution-to-five milliliter 2-heptanone ratio in the presence of ammonium pyrrolidine dithiocarbamate at a pH of 3 to 5. The 2-heptanone extract was aspirated directly into the air-acetylene burner for absorption measurements.

Fourteen lithium hydroxide sample solutions were analyzed in duplicate with the two aliquots of a sample being analyzed at different times. Two solutions were spiked with zinc to give approximately 0.5 and 1.0 μg Zn per ml 2-heptanone—concentrations greater than those of the lithium samples at hand for analysis. These

solutions were analyzed repetitively to give an indication of precision for samples of high zinc content. The resultant data were statistically evaluated. As shown in Table 8, the limit of error (0.95) for a single determination by extraction and atomic absorption measurements varied from ± 10 to ± 22 percent, relative, depending on the amount of zinc present. For the mean of N independent determinations, the limit of error would be:

$$\text{Limit of Error (N determinations)} = \frac{\text{Limit of Error for a Single Determination}}{\sqrt{N}}$$

Table 8
PRECISION OF ANALYSIS FOR ZINC BY THE EXTRACTION METHOD

Zinc Concentration		Number of Aliquots	Standard Deviation	LE (95%) for Single Result	
$\mu\text{g Zn/ml}$ 2-Heptanone	$\mu\text{gs Zn per}$ Gram Sample			Absolute $\mu\text{gs Zn/gm Sample}$	Relative Percent
0.1	3.09	14	0.31	± 0.67	± 22
0.5	15.5	6	0.90	± 2.3	± 15
1.0	29.4	6	1.20	± 3.0	± 10

Applicability of the Method

The extraction method was applied to lithium solutions containing approximately 0.6 gram of lithium per 100 milliliters of solution and 0.01 to 0.2 microgram of zinc per milliliter of solution. This lithium concentration was chosen as compatible with other analytical procedures in use. Increased sensitivity for zinc could be gained readily by extracting from solutions containing greater amounts of sample and by utilizing extraction ratios up to one volume of 2-heptanone to ten volumes of sample solution. Even greater extraction ratios were considered practical but were not investigated.

The extraction procedure, as given, should be readily applicable to water or acid-soluble lithium compounds. More difficultly soluble forms of lithium would require experimentation to dissolve them without attendant zinc contamination. Although the lower limits of analysis were not reached in this work, a practical limit of the extraction method was readily calculated. Assuming the extraction of zinc from 100 milliliters of a lithium chloride solution containing four grams of lithium into 10 milliliters of 2-heptanone, a zinc concentration of 0.02 microgram of zinc per gram of lithium chloride ($0.12 \mu\text{g Zn/gm Li}$) would produce net absorption readings greater than two percent, or 0.01 absorbance unit. Careful experimentation may reveal that even lower detection limits are feasible.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

REFERENCES

- (1) Rowan, J. H.; The Determination of Trace Quantities of Zinc in Lithium Chloride by Derivative Polarography, Y-1320; Union Carbide Corporation-Nuclear Division, Y-12 Plant, Oak Ridge, Tennessee; November 25, 1960.
- (2) Allan, J. E.; "Determination of Zinc in Agricultural Materials by Atomic-Absorption Spectrophotometry", The Analyst, 86, p 530 (1961).
- (3) Willis, J. B.; "Determination of Lead and Other Heavy Metals in Urine by Atomic Absorption Spectroscopy", Analytical Chemistry, 34, p 614 (1962).
- (4) Allan, J. E.; "The Use of Organic Solvents in Atomic Absorption Spectrophotometry", Spectrochimica ACTA, 17, p 467 (1961).
- (5) Malissa, H. and Schoffmann, E.; "Über die Verwendung von Substituierten Dithiocarbamaten III", Mikrochimica ACTA, p 187 (1955).