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# A modification in the determination of reducible sulfur by the tin(II)-strong phosphoric acid method using the LECO$^{tm}$ SC132 Sulfur Analyzer

by

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## Contents

Abstract------------------------------------------------1
Introduction----------------------------------------2
Apparatus-------------------------------------------7
Reagents-------------------------------------------10
Procedure------------------------------------------12
Results and Discussion---------------------------15
Appendix 1- List of Parts-------------------------17
Acknowledgement-----------------------------------22
References-----------------------------------------23

## Illustrations

Figure 1. LECO$^{tm}$ SC132 Sulfur Analyzer.--------------------3
Figure 2. Apparatus - setup--------------------------------8
Figure 3. Apparatus - detail.------------------------------18
Figure 4. Chart - Levels of total sulfur content and reducible sulfur compared.----------------------------21

# Tables

Table 1. Comparison of level of reducible sulfur in inorganic and organic compounds using LECOtm SC132 Sulfur Analyzer.----------------------------------------4

Table 2. Comparison of level of % total sulfur and % reducible sulfur recovered in (dilute 2g/200g CaCO3) organic compounds using LECOtm SC132 Sulfur Analyzer.-5

# A MODIFICATION IN THE DETERMINATION OF REDUCIBLE SULFUR BY THE TIN(II)-STRONG PHOSPHORIC ACID METHOD USING THE LECO$^{tm}$ SC132 SULFUR ANALYZER

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## Abstract

A modified method is presented for the determination of reducible sulfur in organic and inorganic compounds. The method involves the use of a LECO$^{tm}$ SC132 Sulfur Analyzer after the reduction of S to hydrogen sulfide using acidified tin(II) and absorption by 20 mL of alkaline zinc acetate. The absorbed sulfide is precipitated as zinc sulfide, filtered, dried, and the quantity of sulfide determined using the LECO$^{tm}$ SC132 Sulfur Analyzer.

# Introduction

A modified method for determination of reducible sulfur in organic and inorganic compounds, based upon the tin(II)-strong phosphoric acid reduction method described by Shigeru Ohashi (1955), is presented. The purpose of the present study is to establish a practical, simple and rapid method of analysis utilizing the LECO$^{tm}$ SC132 Sulfur Analyzer. Earlier methods consisted of more steps and estimated the sulfur content gravimetrically.

Sulfur in organic compounds is reduced to hydrogen sulfide by heating directly with tin(II) phosphoric acid in a stream of nitrogen gas. The hydrogen sulfide is absorbed by 20 mL of a 2% zinc acetate solution in 12.5N NaOH. The suspension of zinc sulfide in the absorption vessel is then filtered, dried, and the quantity of sulfide is determined with a LECO$^{tm}$ SC132 Sulfur Analyzer (fig. 1).

The ZnS precipitates are combusted in an $O_2$ atmosphere where the sulfide is oxidized to $SO_2$. Moisture and particulates are removed by absorption tubes containing quartz wool and anhydrone. The $SO_2$ gas is then measured by a solid-state infrared detector. The analysis time is 1-2 minutes. The accuracy is +/- 1% of the S content, and the sensitivity is 0.001% (see tables 1 and 2. Also, LECO$^{tm}$ Corporation Instruction Manual, 1980, p.3).

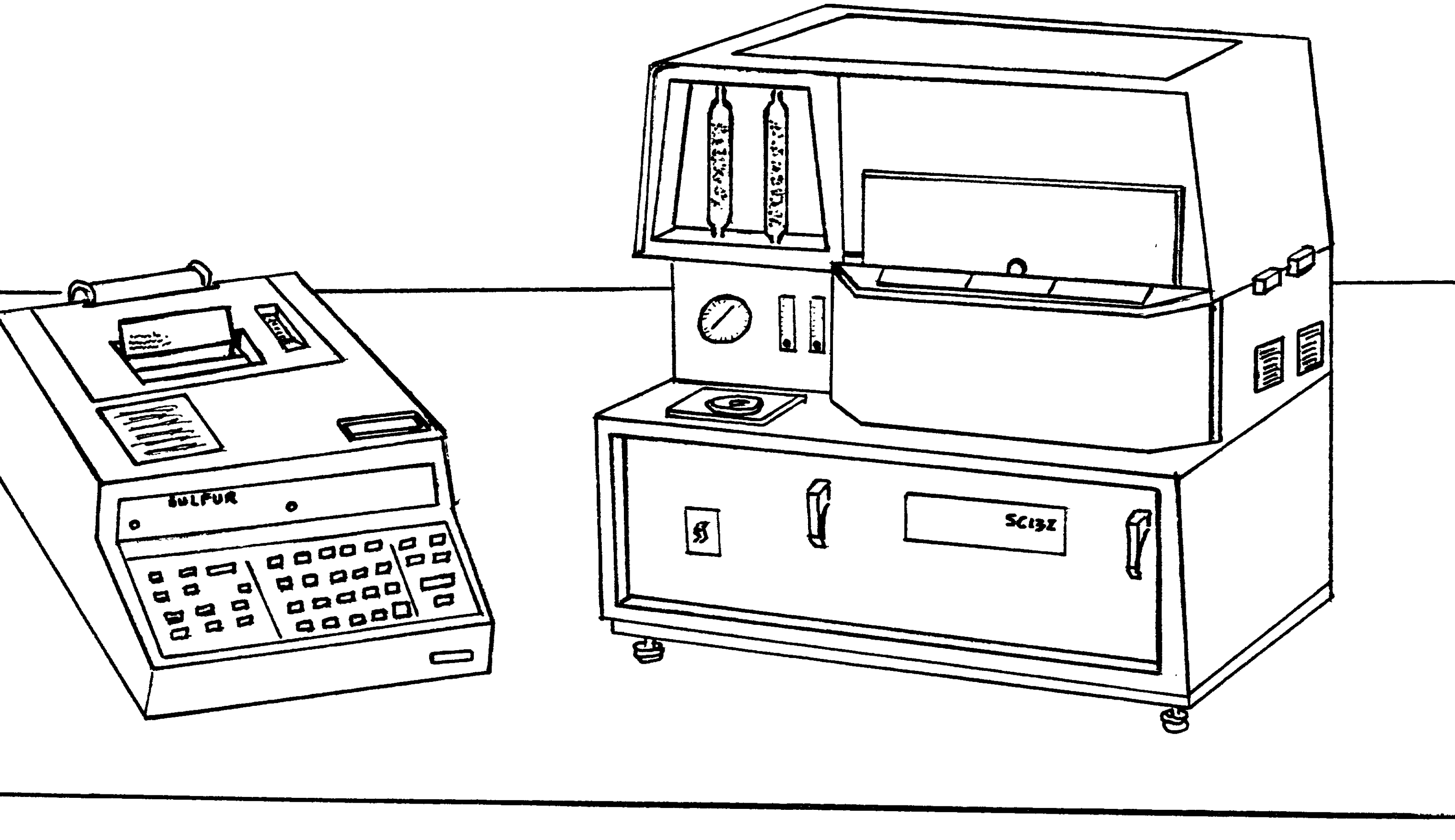

Figure 1. LECO$^{tm}$ SC132 Sulfur Analyzer.

Table 1. Comparison of level of reducible sulfur in inorganic and organic compounds using LECO$^{tm}$ SC132 Sulfur Analyzer.

| Substance | Theoretical Sulfur Content | Total Sulfur Content | | Sample Wt. Mg | Reducible Sulfur Found | |
|---|---|---|---|---|---|---|
| | | Values | Mean | | Values | Mean |
| Pyrite | 43.16 | 45.89 | 49.45 | 11.0 | 44.89 | 45.75 |
| (PS-1 impure) | | 53.00 | | | 46.61 | |
| Methyl- | 9.80 | 9.72 | 9.80 | 20.3 | 8.12 | 9.00 |
| Orange | | 9.88 | | | 9.85 | |
| Cystine | 26.69 | 27.81 | 26.90 | 15.5 | 25.36 | 26.20 |
| | | 25.92 | | | 27.08 | |
| Methionine | 21.49 | 21.52 | 21.60 | 10.5 | 12.81 | 13.67 |
| | | 21.65 | | | 14.53 | |
| Basic Slog- | 0.45 | 0.44 | 0.46 | 200.00 | 0.39 | 0.39 |
| 248/1 | | 0.47 | | | 0.38 | |
| Basic Slog- | 0.30 | 0.30 | 0.30 | 200.00 | 0.30 | 0.30 |
| 249/1 | | 0.29 | | | 0.30 | |

Table 2. Comparison of level of % total sulfur and % reducible sulfur recovered in (dilute 2g/200g $CaCO_3$) organic compounds using LECO$^{tm}$ SC132 Sulfur Analyzer.

| Substance | Theoretical Sulfur Content | Total Sulfur Content | Sample Wt. Mg | Reducible Sulfur Found |
|---|---|---|---|---|
| Cystine | 0.267 | 0.260 | 200 | 0.265 |
| | | 0.268 | 200 | 0.250 |
| | | 0.266 | 200 | 0.266 |
| | | 0.275 | 200 | 0.270 |
| | | 0.268 | 200 | 0.264 |
| | | 0.330 | 200 | 0.277 |
| | | 0.251 | | |
| | | 0.249 | | |
| Mean | | 0.271 +/- .025 | | 0.265 +/- .009 |

The recovery and determination of reducible sulfur in pyrite, methyl orange, cystine and methionine, was studied by this new procedure. The pyrite used was the Freiburg standard, PS-1, a quartz-pyrite mixture certified to contain 43.16 wt. percent S and 40.36 wt. percent Fe (Schrön, Rösler, and others, 1975). The methyl orange, cystine and methionine were laboratory shelf reagents.

## Apparatus

The apparatus used in this study is per USGS procedure for coal analysis, and is shown in fig. 2. Five or more can be easily handled simultaneously.

Nitrogen is bubbled through the reagent in the reaction vessel, passed through the condenser and into the absorption (recovery) vessel. The rate of bubbling in this vessel may be controlled by raising or lowering the laboratory jack (I).

The size of the tip of the nitrogen inlet tube of the reaction vessel is about half that of the nitrogen inlet tube in the absorption vessel, which is optimally covered by a gas dispersion tube. This produces good agitation of the mixture in the reaction vessel without excessive nitrogen flow through the absorption vessel. The air in the apparatus must be displaced by nitrogen before hydrogen sulfide is released from the sample solution. Incomplete removal of air leads to low results.

Note: Strong phosphoric acid has a strongly corrosive action against glass at high temperature. After being used many times, the bottom of the vessel (A) will become so thin that it must be thickened by heating with a gas burner.

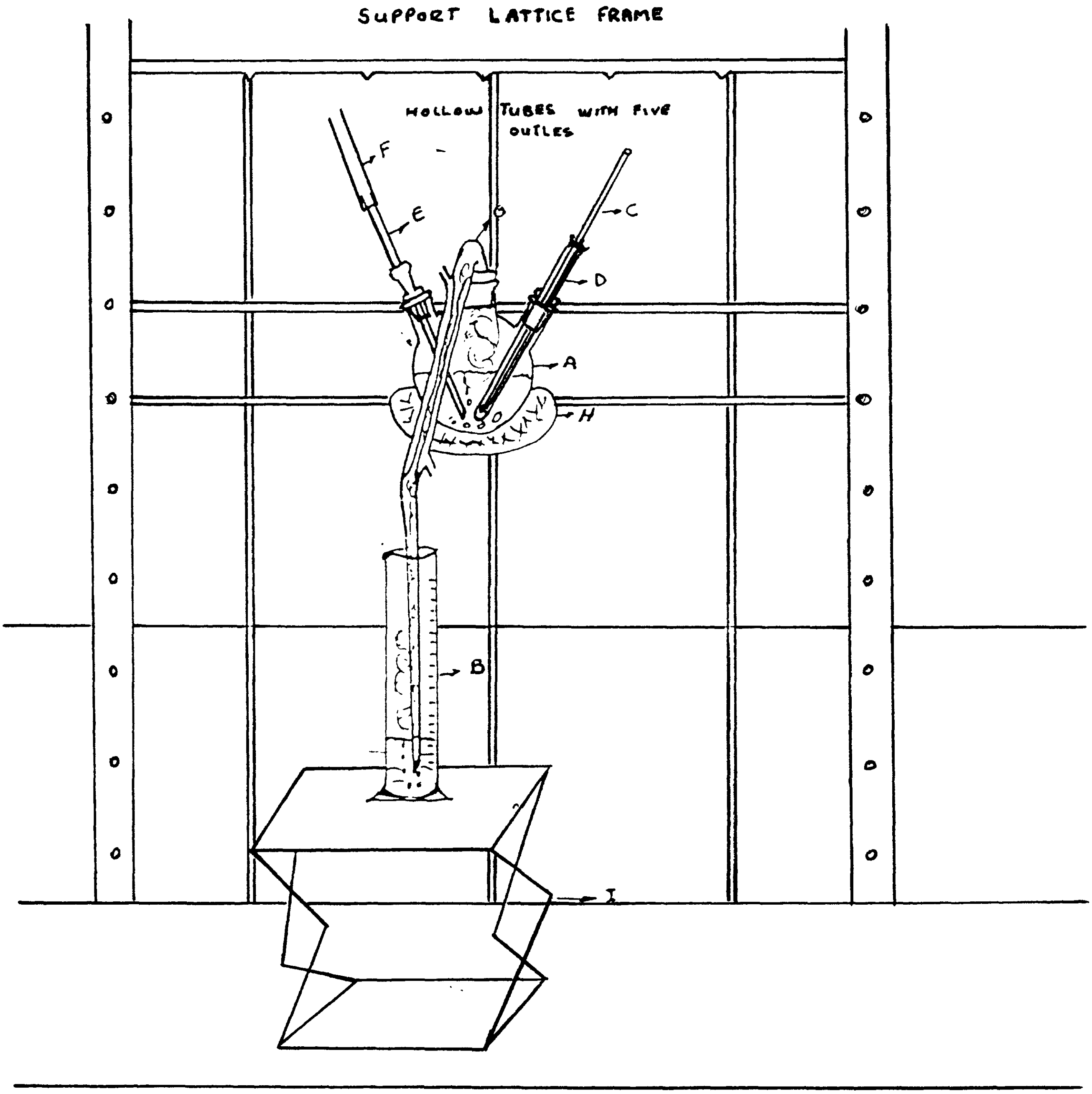

Figure 2. Apparatus - setup

Figure 2. Apparatus - Setup.

1. Reaction vessel (three-neck round bottom flask (A)).

2. Absorption vessel (100 mL graduated cylinder (B)).

3. An air cooled condenser (G) closing the center neck of the reaction vessel. The spout at the end of the condenser is placed inside the absorption vessel.

4. A laboratory jack (I), which may be raised or lowered to adjust the flow of nitrogen in the absorption vessel.

5. Bubble tube (E & F) in one side neck of the reaction vessel. Each of the flasks' bubble tubes is connected to a common tube that feeds nitrogen into all the reaction vessels.

6. The middle (in this example, third) flask in the setup has a thermometer in a protector (C & D) inserted in the other side neck, while the other four flasks have a stopper in the other side neck.

7. Hemispherical electric heating mantles (H) hold each of the reaction vessels.

## Reagents

All chemicals and gases are reagent grade.

1. Ortho-phosphoric acid AR: 85%, S.G.:1.7, B.P.: 260° C.

2. Stannous chloride: dihydrate crystal, A.C.S..

3. 20% Zinc acetate solution: Dissolve 200 g $Zn(C_2H_3O_2)_2$ in 800 mL $H_2O$.

4. 12.5N NaOH solution.

5. Nitrogen gas cylinder and gauge.

6. Oxygen gas cylinder and gauge

7. $V_2O_5$ flux reagent.

8. LECO$^{tm}$ Corporation standards used for calibration: 0.52% S; 1.10% S; 1.77% S; 2.97% S and 3.65% S.

9. Tin(II)-strong phosphoric acid reagent.

Stock solution: Place 20 g of the extra pure $SnCl_2.2H_2O$ in the bottom of a three-neck round-bottom 250-300 mL flask and dissolve in 386 mL strong ortho-phosphoric acid (AR 85% SG 1.7). The mixture is heated at 280° C. in a stream of $N_2$ gas. This will expel the hydrogen chloride in the mixture, as well as the trace of sulfur contained in the tin(II)-chloride.

The liberated gas is removed into a graduated cylinder (B) absorption vessel with 20 mL of the absorbent reagent solution alkaline zinc acetate, and used as a blank. Heat the mixture to $280^{\circ}$-$300^{\circ}$ C., and continue heating for another 30 minutes. At the end of this time, turn off the heat, keeping $N_2$ gas going through the reagent until it is cool enough to be transferred into a 300 mL Erlenmeyer flask, and place it in a desiccator with $CaCl_2$ desiccant for future use as stock solution. The reagent can be stored for a month without any change in composition if it is kept in an air-tight container.

10. 2% alkaline zinc acetate solution (prepare just before use): Add 30 mL of 20% stock solution of zinc acetate to 285 mL water in a 400 mL beaker. Place a stirring rod in the solution and place the beaker on a hot plate. Stir the solution, and while stirring, add 10 mL of 12.5N NaOH.

11. 30% hydrogen peroxide solution - mixed with 12.5N NaOH in a 1:1 ratio for cleaning glassware.

## Procedure

Blank determinations are made whenever a new batch of any of the reagents is used in the analysis, for use as blank correction. A blank from the current batch of the reductant reagent should be prepared at the same time as the samples, in the same volume.

In addition, a known sulfur standard compound should be analyzed with the unknown samples. The standard to be used depends upon the total sulfur contained in the samples to be analyzed.

1. Weigh accurately 10 to 20 mg of sample into the reaction vessel, depending upon expected sulfur content. (If the sample contains 5% or less total S, as much as 200 mg of sample can be used. To avoid exceeding instrumental limitations, it is best to use a sample of 20 mg if it contains 5-20% total sulfur, and 10 mg if the total S is greater than 20%.)

2. Add 15 mL of the tin(II) phosphoric acid reagent.

3. Add 20 mL of the warm alkaline 2% $Zn(C_2H_3O_2)_2$ solution to the absorption vessel.

4. Start the flow of nitrogen gas through the reaction vessel and purge for about 10 minutes. The passage of nitrogen should be rapid enough to cause strong agitation of the surface of the liquid in the reaction and absorption vessels. Reduce the flow of nitrogen to a rate of 3-5 bubbles per second in the absorption vessel. Maintain this rate until the completion of the reaction.

5. Heat the reaction flasks with electric heating mantles.

6. Heat at $280\text{-}300^{\circ}$ C for 30 minutes. Turn off the heat but continue flowing nitrogen gas through the reaction vessel until it cools to room temperature.

7. Remove the absorption vessel and the condenser from the reaction vessel.

8. Using a wash bottle containing water, thoroughly wash down any material adhering to the outer tip and inside of the condenser three times, and add the rinses to the collector vessel containing the precipitated ZnS.

9. Vacuum filter the alkaline mixture through a cellulose triacetate vacuum filter, 0.45 micron, 47 mm diameter.

10. Place the wet filter paper on a watch glass and heat it in a drying oven at 110° C overnight.

11. Transfer the dried precipitate and the filter paper to a LECO$^{tm}$ combustion boat.

12. Add about 0.5 g of reagent grade $V_2O_5$ to cover the sample.

13. Calibrate the LECO$^{tm}$ SC132 Sulfur Analyzer in accordance with the instructions in the manual. Then low-level LECO$^{tm}$ coal standards (less than 1 percent S) and blanks are run until the baseline of the SC132 gives a consistent readout. Determine % S in the samples using the LECO$^{tm}$ SC132 Sulfur Analyzer.

## Results and Discussion

Analyses of several known organic and inorganic sulfur compounds were completed using this modified method. The results obtained are shown in tables 1 and 2. It is clear that reducible sulfur in compounds such as methyl orange, cystine, and pyrite PS-1 is easily determined by this modified method, with +/- 90% recovery (fig. 4). The results obtained for methionine show more variation. Methionine's sulfur is not further reducible and should not be recoverable by this method. In all likelihood, the shelf compound utilized was aged and somewhat oxidized. Hence, those results are discounted.

The time variable: The experiment showed that the reduction of sulfur is completed after a few minutes. The time needed to transfer the $H_2S$ into the absorbing solution of alkaline $Zn(C_2H_3O_2)_2$ obviously depends on the rate of nitrogen flow.

The apparatus for the preparation of the reagent and the reduction of the sulfur are illustrated. Determinations of sulfur in various organic and inorganic sulfur compounds were carried out by this modification, and satisfactory results were obtained.

The advantages of this method are that solid samples of organic compounds can be treated directly in the reaction vessel, with satisfactory recovery of the reducible sulfur. The need for iodimetric determination is eliminated. In addition to the savings in time, it was found that use of the LECO$^{tm}$ SC132 Sulfur Analyzer permits determination of smaller quantities of sulfide than the gravimetric method.

## Appendix 1- List of Parts

The quantity of individual items required depends upon the number of samples to be analyzed.

1. Support lattice frame to be used as a rack for sulfur extraction equipment (fig. 3).

2. Hollow tube, with five outlets and one inlet for nitrogen (fig. 3).

3. Tygon tubing to fit outlet and inlets of above.

4. Flowmeter to control nitrogen flow (fig. 3).

5. Three-neck round-bottom 200 mL flasks. The two outside necks have ground glass joints 19/38 and the center neck has ground glass joint 24/40 (fig. 2).

6. Hemispherical electric heating mantles to fit above round-bottom flasks (fig. 3).

7. Heating mantle racks (fig. 3).

8. Electric extension with five outlets.

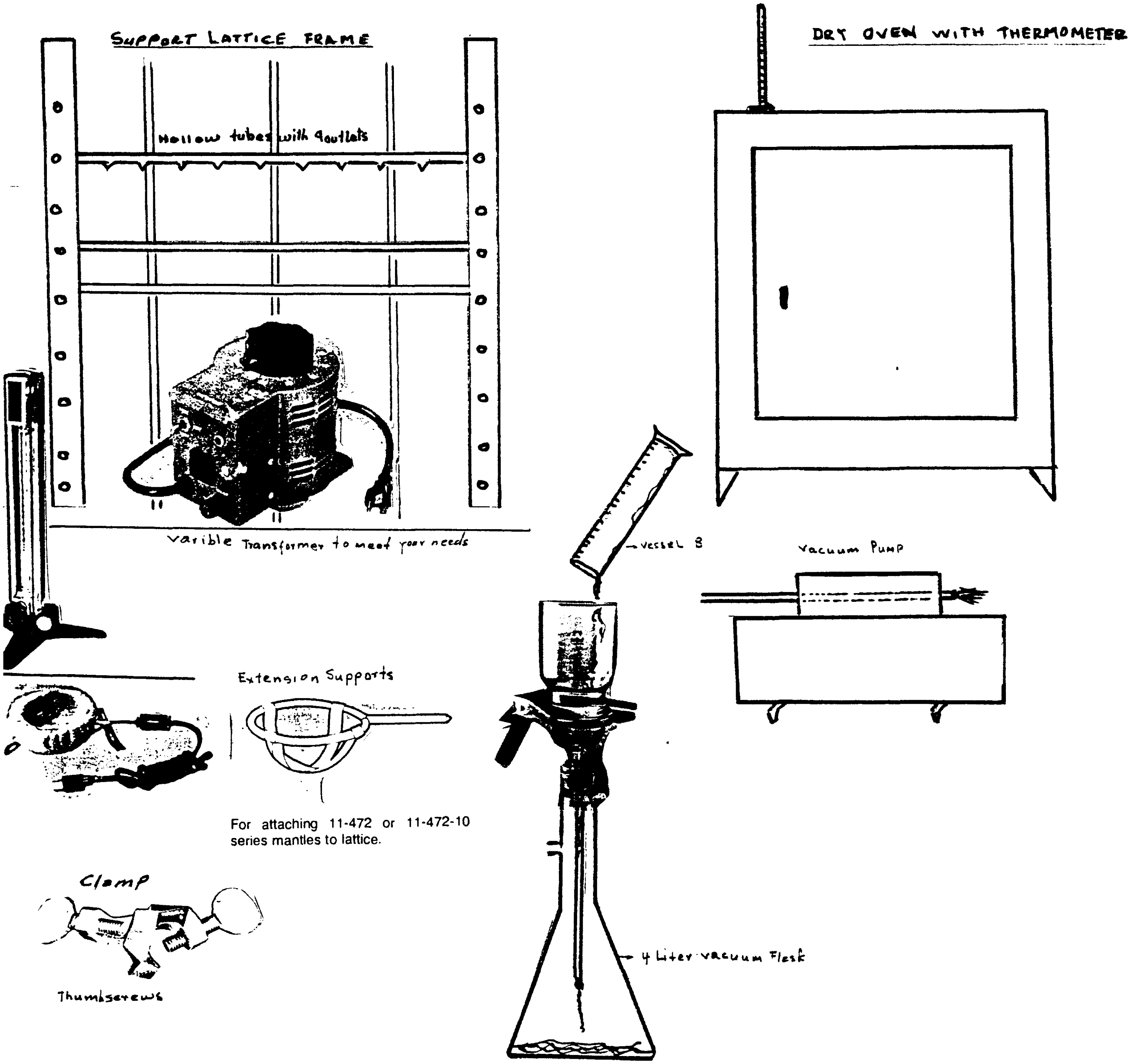

Figure 3. Apparatus - detail.

9. Variable transformer (0-120/140 volts), as heater control, controlling electric current to the mantles (fig. 3).

10. Graduated cylinders, 100 mL (fig. 2).

11. Laboratory support jacks to raise and lower graduated cylinders (fig. 2).

12. Two thermometers with thermometer protectors (10°-0°-360°C.).

13. Condensers (fig. 2) with ground glass joints 14/35.

14. Pyrex ground glass reducing adapters, outer joints 19/38, inner joints 10/30. (fig. 2).

15. Pyrex reducing adapters 19/38 to 10/30.

16. Vacuum pump 115V (fig. 3).

17. Four-liter vacuum flask with fritted glass filter, filter funnel and clamp (fig. 3).

18. Pyrex tapper inner ground glass joints 10/30 with tube extension. ODxL: 8x120 mm (fig. 2).

19. Pyrex ground glass stoppers 19/38.

20. Cellulose triacetate vacuum filters - pore size 0.45 micron, 47 mm diameter.

21. Drying oven and thermometer for drying oven (fig. 3).

22. Watch glass - 5 centimeters diameter (to hold the wet filter paper with the precipitated zinc sulfide when placed in the oven).

23. Stirring bar and 400 mL beaker.

24. Small hot plate with temperature control and magnetic stirrer.

25. LECO$^{tm}$ SC132 Sulfur Analyzer.

26. LECO$^{tm}$ Sulfur Analyzer combustion boats.

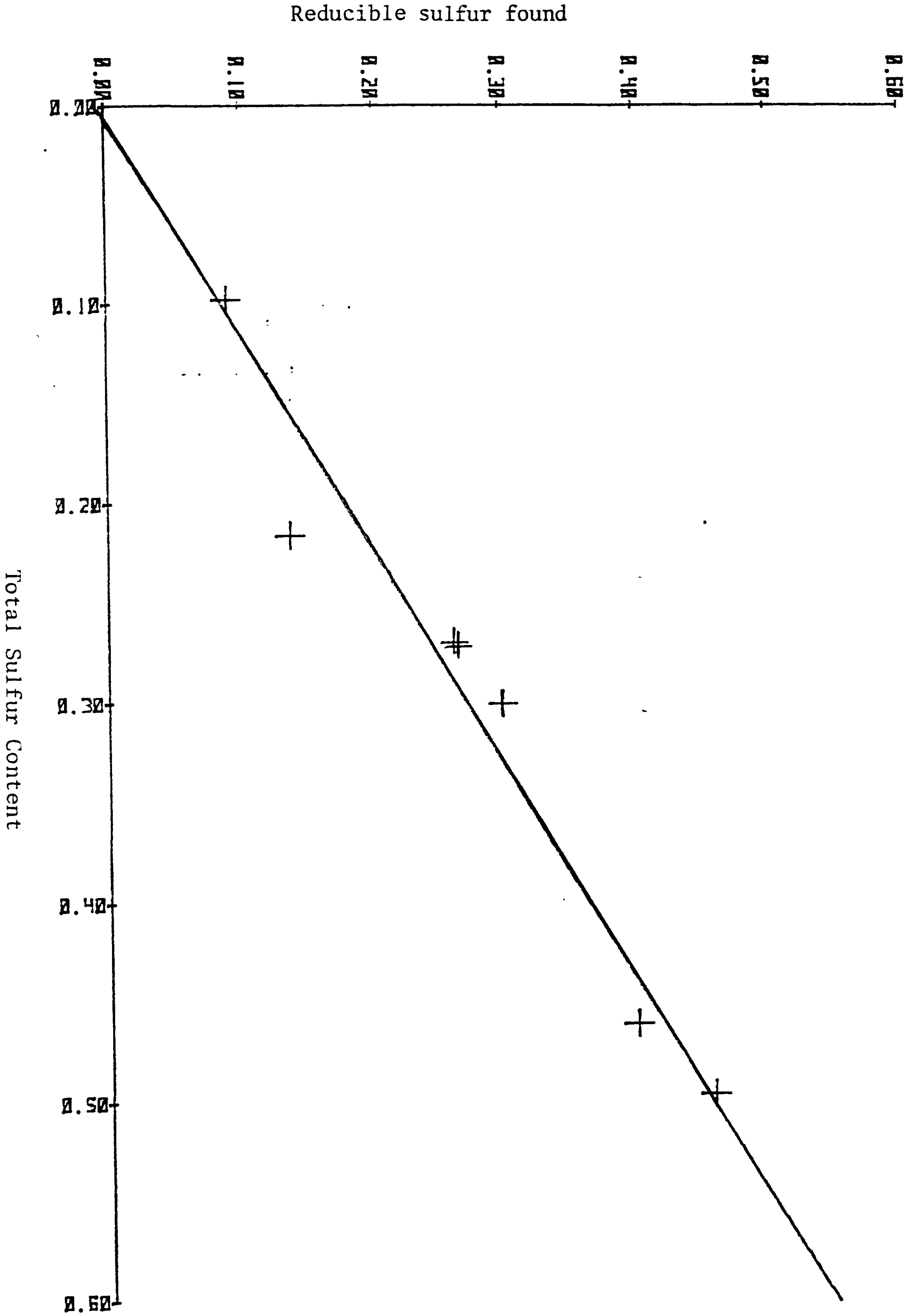

Figure 4. Chart - Levels of total sulfur content and reducible sulfur compared.

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