

DETERMINATION OF TRACE MERCURY IN  
SOIL, ROCK AND VEGETATION

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirement for the degree of Master of Science.

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ABSTRACT

A rapid method for the accurate determination of mercury in the parts per million and parts per billion range is described. The procedure eliminates previously problematic interferences due to organic matter in the sample. The pulverized sample is subjected to a nitric-perchloric acid digestion and mercury is extracted into an organic solvent containing dithizone. The extracted mercury is measured by atomic absorption spectrophotometry in the organic phase. Atomizing the mercury in the organic media results in an eight-fold signal enhancement and the extraction separates mercury from common interfering species. The lower limit of detection with this method is  $0.05 \mu\text{g}$ .

TABLE OF CONTENTS

List of Figures.....	v
List of Tables.....	vi
Acknowledgements.....	vii
Introduction.....	1
Mercury in the Natural Environment.....	1
Procedures for Determining Mercury.....	2
Experimental Work.....	5
Improving Sensitivity in Mercury Analysis.....	5
Instrumentation.....	9
Reagents.....	12
Calibration.....	12
Procedure.....	13
Discussion.....	16
Analysis of Mercury in Rock and Soil Media.....	16
Analysis of Mercury in Vegetation.....	24
Conclusions.....	27
Appendix.....	29a
Bibliography.....	30

LIST OF FIGURES

Figure

1.	Extraction efficiency of silver dithizonate, gold dithizonate and palladium dithizonate into MIBK as a function of pH.....	10
2.	Extraction efficiency of mercuric dithizonate into MIBK as a function of pH.....	11
3.	Typical calibration curves for mercury determinations.....	15
4.	Mercury analysis of soil samples of varying organic content using a Lemaire SV mercury detector, an unspecified technique and the proposed method.....	23

LIST OF TABLES

## Table

1.	Concentration of mercury in various rock types.....	1
2.	Mercury analysis of six rock and soil samples.....	17
3.	Mercury analysis of six rock and soil samples showing replicate analysis, mean values and standard deviations.....	18
4.	Results obtained on standard samples.....	19
5.	Mercury analysis of some Arizona soil samples.....	21
6.	Mercury analysis of some soil samples of varying organic content.....	22
7.	Mercury analysis of grain seed samples.....	26
8.	Effect of various cations on the direct determination of mercury in aqueous - acid solution by atomic absorption.....	29b
9.	Extraction efficiency of silver dithizonate, gold dithizonate, mercury dithizonate and palladium dithizonate as a function of pH.....	29c

ACKNOWLEDGEMENTS

I wish to express my gratitude to the following people whose assistance was greatly appreciated while completing this thesis.

To Dr. Ramon E. Bisque, my thesis advisor, whose encouragement, humor and common sense make graduate study a most enjoyable experience.

To Dr. George B. Lucas and Dr. Kenneth W. Edwards, who served on my thesis committee and often provided suggestions and insights.

To Luba D. Pyrih, my wife, for much needed encouragement throughout my graduate work.

To the graduate students of the Chemistry Department with whom many an hour was spent at coffee.

I would also like to thank the Colorado School of Mines Foundation, Inc. and the U. S. Geological Survey for financial assistance which enabled me to complete this work and all the individual groups that have contributed to CHEMLAUNCH.

INTRODUCTIONMercury in the Natural Environment

The average crustal abundance of mercury is 0.08 ppm, considerably below zinc (70 ppm), copper (13 ppm) or uranium (1.8 ppm) and slightly above that of gold (0.004 ppm) or silver (0.07 ppm) (Mason, 1966). The mercury content of various rock types is summarized in table 1.

Table 1. Concentration of mercury in various rock types.

Rock Type	Krauskopf (1955) (ppm)	Mason (1966) (ppm)
Igneous	0.06	0.08
Carbonates	0.03	0.04
Sandstones	0.03	0.03
Shales	0.40	0.40

Aidin'yan, Troitskii and Belavskaya (1964) suggest that the mercury content of soils ranges from zero to 10.0 ppm in areas devoid of mercury mineralization. Such concentrations are partially due to the upward diffusion of gaseous mercury into the soil horizon, with subsequent interstitial trapping of the mercury by mineral and rock particles of the soil (Hawkes and Webb, 1962). In a porous medium, mercury vapor

will move for relatively great distances from the source.

Anomalously high concentrations of mercury in rock or soils may indicate hidden or poorly exposed mineralization. Several investigators (Hawkes and Williston, 1962; Williston, 1964; Delavault and Barakso, 1966) have suggested that extensive mercury halos exist around sulfide deposits, and that detection and evaluation of such halos may prove valuable in locating sulfide mineralization. For example, Ozerova (1959) found anomalous mercury halos 1 to 2 kilometers wide embracing lead-zinc deposits occurring in zones less than 100 meters wide.

#### Procedures for Determining Mercury

Instrumentation and procedures currently exist for the detection of macro amounts of mercury. They include: volumetric (Saxena, 1967) and photometric (Pietrzyk and Belisle, 1965) procedures, atomic fluorescence (Mansfield, Winefordner and Veillon, 1965) and radiochemical methods (Samsahl, 1967).

Colorimetric methods are available for the determination of traces of mercury (Irving, Andrew, and Risdon, 1949; Sandell, 1959; Hinkle, Leong, and Ward, 1966). Of the colorimetric reagents available, diphenylthiocarbazone ("dithizone") is the most popular because of its sensitivity for mercury. To achieve selectivity with dithizone, careful control of pH and the addition of complexing agents are necessary (Friedeberg, 1955; Sandell, 1959). Unfortunately,

organic matter in the sample may interfere with the determination by causing discoloration of the reagent (Ward and McHugh, 1964).

Several instruments are available for the determination of microgram and nanogram quantities of mercury in natural materials. The various methods used have different degrees of reliability, sophistication and portability (Azzaria and Webber, 1969). In most instrumental techniques the determination of mercury vapor produced by direct heating of the sample is based on mercury's absorption of ultra-violet radiation of wave length  $2537 \text{ \AA}$  (Woodson, 1939; Vaughn and McCarthy, 1964; Williston and Morris, 1965; Vaughn, 1967). However, organic-rich samples have presented difficulties to most of these instrumental methods because a number of organic vapors produced when soils are heated for mercury analysis absorb the  $2537 \text{ \AA}$  radiation (Hanson, 1941). Moreover, smoke and incompletely burned organic matter may pass into the absorption chamber along with mercury and interfere with the analysis.

Atomic absorption spectrophotometry has found some limited use in trace mercury analysis (Hingle and Kirkbright, 1967; Tindall, 1967; Hatch and Ott, 1968). However, analysis of natural materials for mercury in aqueous-acid solutions commonly proves difficult by atomic absorption spectrophotometry. Such determinations lack the sensitivity required for trace analytical work, and are subject to interferences from alkali and alkaline-earth metals and other metal cations present in the sample matrix. A need exists for an analytical

technique that will give accurate, rapid and inexpensive geochemical analyses for mercury in the parts per million and parts per billion range.

## EXPERIMENTAL WORK

### Improving Sensitivity in Mercury Analysis

Liquid-liquid solvent extraction has been used for some time as a method of separation in analytical procedures (Morrison, 1950; Morrison and Freiser, 1957; Chaberek and Mortell, 1959) and recently found applicable to atomic absorption spectrophotometry.

Simple metal ions, because of their highly ionic nature, are rarely soluble in non-polar organic solvents. In essentially all metal extraction systems some or all the water molecules coordinated to the metal ions must be removed before extraction into a non-polar solvent can occur. The formation of an uncharged species is usually a prerequisite for extraction (Martell and Calvin, 1952; Morrison and Freiser, 1957).

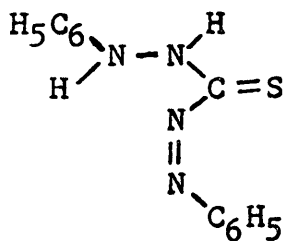
Chelating reagents play an important role in the extraction of metal ions because they comprise an impressive body of useful extraction agents. Such chelating reagents as ammonium pyrrolidine dithiocarbamate, cupferron, dithizone and 8-quinolinol easily replace coordinated water from many metals to form neutral essentially covalent, chelate compounds which are more soluble in organic solvents than in water.

Many such solvent extraction procedures have been

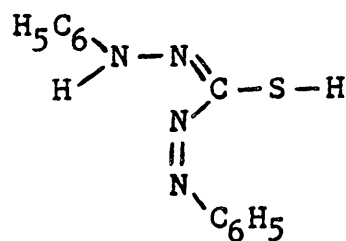
used with atomic absorption spectrophotometry to improve detection limits and sensitivity for a number of metals. Their enhancement of useful signal in atomic absorption spectrophotometry is well known (Allan, 1961; Robinson, 1962). For example, total chromium in fresh water was determined by atomic absorption with prior chelation by ammonium pyrrolidine dithiocarbamate and extraction into methyl iso-butyl ketone (Midgett and Fishman, 1967). Roosels and Vanderkeil (1968) determined lead in urine after extraction with dithizone in chloroform and by using atomic absorption, Feldman and Dhumwad (1962) determined mercury in nuclear reactor fluids by chelation and extraction of mercury as the mercuric dithizonate, into a solution of cyclohexane and methyl iso-butyl ketone.

Dithizone forms colored dithizonates with 17 metals and has been used extensively as a chelating agent in colorimetric analysis (Sandell, 1959). It will selectively chelate and extract Ag (I), Au (III), Cu (II), Hg (II), Pd (II) and Pt (II) from dilute acid solution.

The compound exhibits tautomerism:



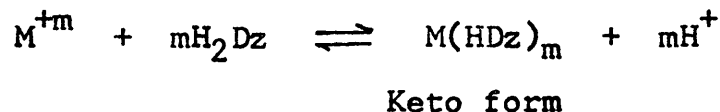
Keto form



Enol form

and behaves as a monobasic acid up to a pH of 12. The mercapto

group is involved in metal complex formation according to the reaction:

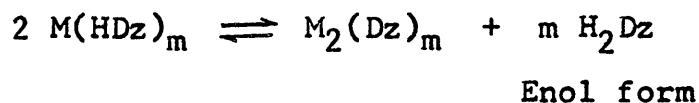


where the metal ion ( $M^{+m}$ ) is initially in an aqueous phase and the dithizone ( $H_2Dz$ ) and metal dithizonate ( $M(HDz)_m$ ) is in an organic solvent phase.

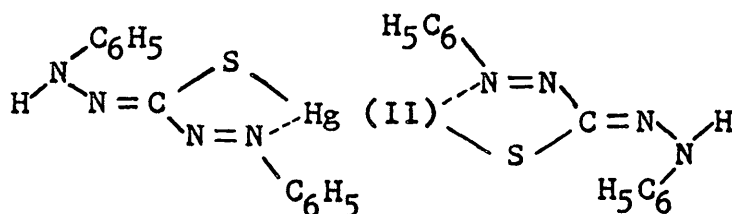
Hydrogen ion concentration of the aqueous solution governs the formation of the metal dithizonate and controls extraction efficiency. This is evident from the simple equilibrium:

$$K = \frac{(M(HDz)_m) (H^+)^m}{(M^{+m}) (H_2Dz)^m}$$

Some metals, notably Cu, Ag, Au, Hg, Bi and Pd, form the enol complex at a higher pH range or in a deficiency of reagent in which another proton is replaced:



The keto dithizonates are of far greater analytical utility than their enol counterparts which are less stable and less soluble in organic solvents. The probable structure for the keto mercury complex is



The enol complex would probably involve dithizone as a tridentate chelating agent (Morrison and Freiser, 1957, p. 173-177).

Geiger and Sandell (1953) studied Cu (II) - dithizone equilibria involved in the extraction of Cu (II) from a water solution by dithizone in carbon tetrachloride. Irving, Andrew and Risdon (1949) investigated the influence of acidity, halide-ion concentration and shaking time upon the extractability of mercury and copper by dilute solutions of dithizone in both chloroform and carbon tetrachloride.

Chloroform and carbon tetrachloride are unsuitable as solvents for solvent extraction procedures with atomic absorption spectrophotometry; aspirating these solvents will cause an unstable flame and decrease the signal to noise ratio of the spectrophotometer. Esters and ketones, immiscible with water, are perhaps the best solvents that can be used; they give steady and complete combustion. Methyl iso-butyl ketone ("MIBK") has been used in a number of procedures.

Dithizone was found to be quite soluble in methyl iso-butyl ketone and capable of chelating and extracting Ag (I), Au (III), Cu (II), Hg (II), Pd (II) and Pt (II) from dilute perchloric acid solution. Optimum pH conditions were determined for Ag (I), Au (III) and Pd (II) extractions (fig. 1) and for Hg (II) extraction (fig. 2).

The dithizone - methyl iso-butyl ketone extraction procedure can be utilized for atomic absorption spectrophoto-

metric determinations of microgram and nanogram concentrations of mercury in natural samples (Pyrih and Bisque, 1969). Mercuric ions taken into solution by hot oxidizing acid digestion are chelated by dithizone and extracted as mercuric dithizonate into methyl iso-butyl ketone. The extracted mercury in the immiscible organic layer is measured by atomic absorption.

The lower limit of detection with this technique is  $0.05\mu\text{g}$  of mercury. Fifty parts per billion of mercury can be detected in a one gram sample. Increasing sample size will lower the detection limit to a few parts per billion which is well below the average abundance of mercury in crustal rock, 0.08 parts per million (Mason, 1966, p. 46).

### Instrumentation

A Perkin-Elmer Model 303 atomic absorption spectrophotometer equipped with a three-slot Belling burner was used in the present investigation. Because of excessive voltage fluctuations during the day, analyses were primarily performed in the evenings. Experimental conditions are listed below:

Wave length	254 $\text{m}\mu$
Lamp current	10 ma
Slit setting	5
Scale expansion	10x
Meter response	2
Acetylene flow	3
Air flow	9

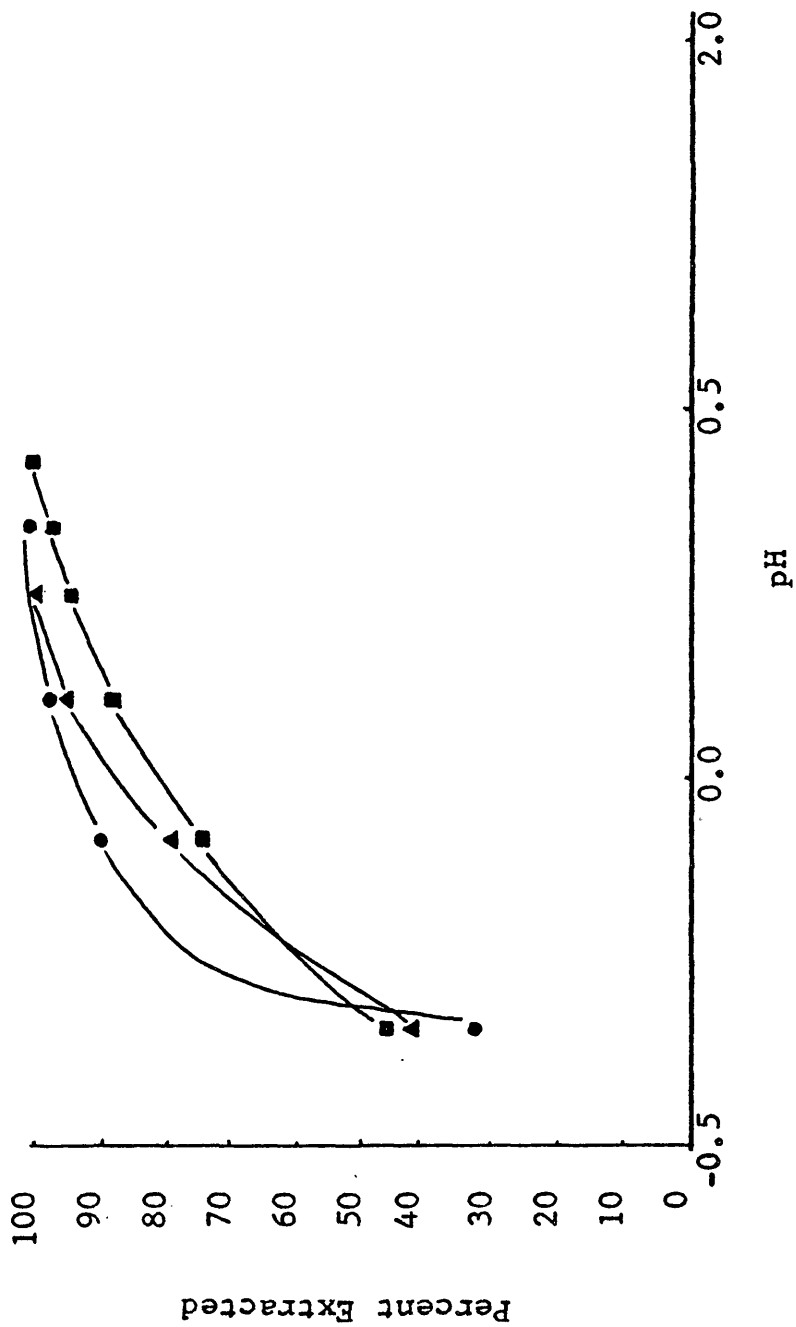


Figure 1. Extraction efficiency of silver dithizonate ( $\blacktriangle$ ), gold dithizonate ( $\bullet$ ) and palladium dithizonate ( $\blacksquare$ ) into MIBK as a function of pH.

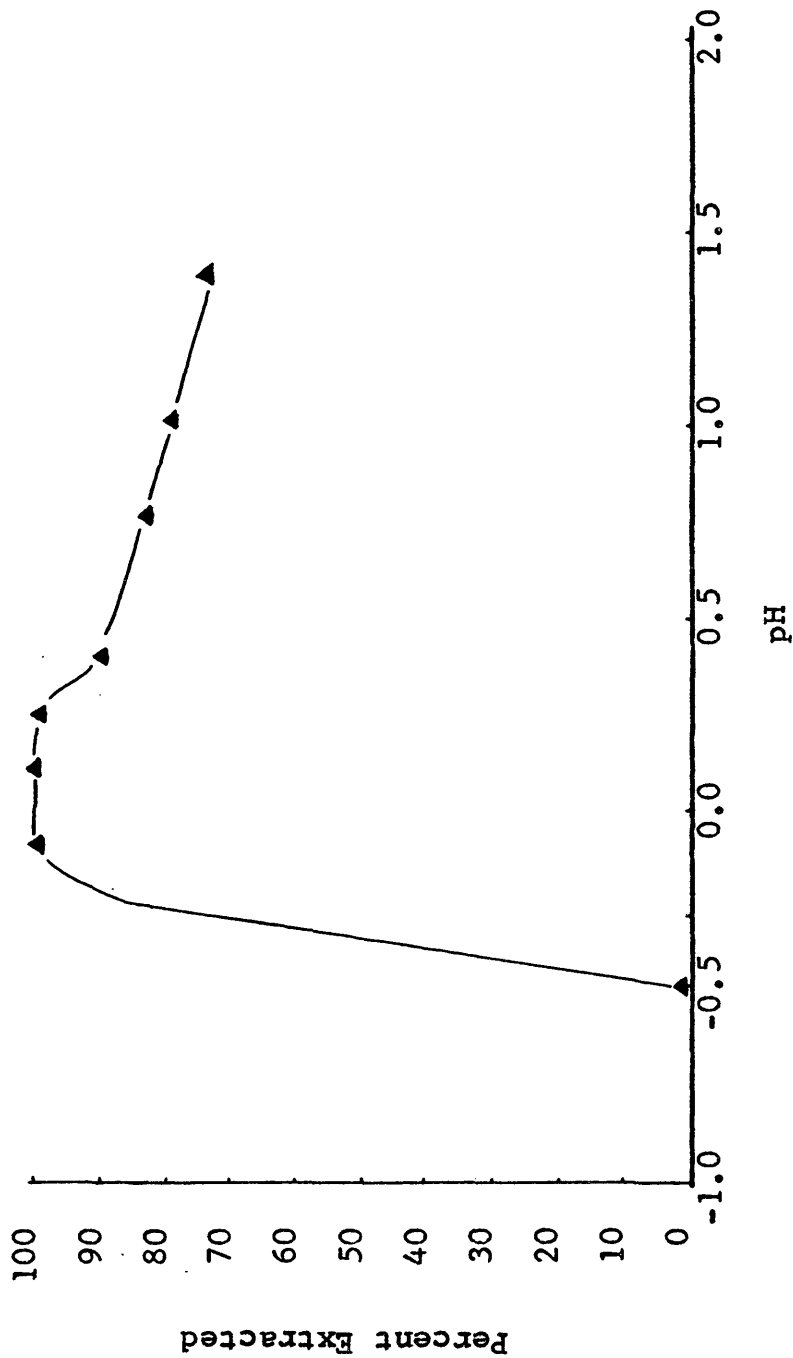


Figure 2. Extraction efficiency of mercuric dithizonate into MIBK as a function of pH.

### Reagents

1. Dithizone solution: 0.005 percent by weight per unit volume, reagent-grade dithizone in reagent-grade methyl iso-butyl ketone. This solution should be prepared fresh daily.
2. Methyl iso-butyl ketone, reagent-grade.
3. Nitric acid, concentrated, reagent-grade.
4. Perchloric acid, concentrated, reagent-grade.
5. Standard mercury solution, 1000  $\mu\text{g}$  per ml: dissolve 0.1354 g reagent grade mercuric chloride ( $\text{HgCl}_2$ ) in 100 ml 0.5 M  $\text{H}_2\text{SO}_4$ . From this stock solution other standards are prepared by dilution with 0.5 M  $\text{H}_2\text{SO}_4$ . Dilute standards should be prepared daily.

### Calibration

Aliquots of standard mercury solutions containing 0.05 to 20.0  $\mu\text{g}$  of mercury are transferred to culture tubes (20- x 200-mm). Two ml concentrated perchloric acid are added to each tube and then diluted with demineralized water to a total volume of 30 ml (pH 0.1). Exactly 5 ml of dithizone solution is then pipetted into the tubes. Solutions are shaken manually for 30 seconds. The immiscible organic layer is then aspirated into the spectrophotometer and the absorbance measured at 254  $\text{m}\mu$  (fig. 3).

Before each determination the zero reading is checked

by aspirating a blank organic solution prepared identically but with no mercury added. Lower limit of detection with this method is  $0.05\mu\text{g}$  of mercury (fig. 3).

### Procedure

A one gram sample (-100 to -250 mesh) is transferred into a dry culture tube. To this is added one ml concentrated nitric acid and two ml concentrated perchloric acid. The sample is then digested for at least an hour on a hot plate. The literature regarding the use of perchloric acid with organic rich materials should be reviewed (Smith, 1953). The temperature of the hot plate should be controlled during digestion ( $200^{\circ}$ - $230^{\circ}\text{C}$ ) to prevent the escape of dense white perchloric acid fumes that may lead to loss of mercury. For this reason, tall culture tubes are recommended in the digestion procedure. At the specified digestion temperature perchloric acid fumes condense on the upper walls of the culture tube.

After cooling, the sample is diluted with demineralized water to a total volume of 30 ml (pH 0.1). Five ml of dithizone solution is added to the sample and the tube shaken for 30 seconds to extract the mercury into the organic layer. The immiscible organic layer is aspirated and the absorbance is measured against a blank solution.

If lower detection limits are desirable, sample size may be increased. If necessary, the procedure may be modified

and larger volumes of acids used.

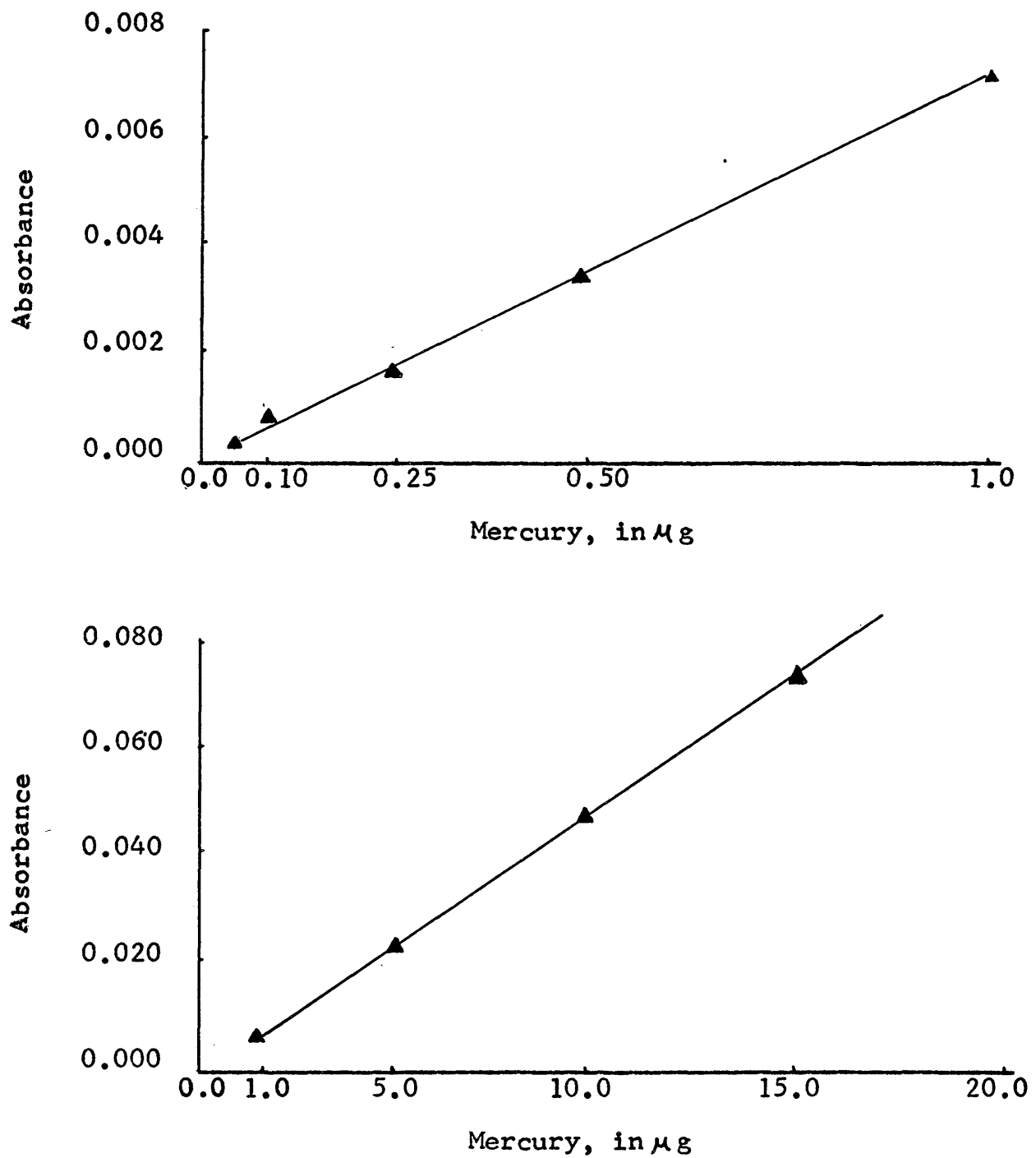


Figure 3. Typical calibration curves for mercury determinations.

## DISCUSSION

### Analysis of Mercury in Rock and Soil Media

The validity and usefulness of the proposed new method were evaluated by analyzing a set of six samples (table 2) representing several rock and soil types that had been analyzed by the Vaughn-McCarthy method (Vaughn and McCarthy, 1964). Because of discrepancies between values obtained by the Vaughn-McCarthy method and those obtained by this new method, the possibility that the differences might be due to incomplete digestion of the sample by the nitric-perchloric treatment was investigated. By taking the dried digestion residue from sample nos. 2 and 5 (table 2) and analyzing for mercury with a Lemaire SI mercury detector this possibility was negated. The residues were found to contain less than 0.5 parts per million.

The precision of the method was determined by replicate analysis of the same six samples (table 3). The accuracy of the proposed method was assessed by reanalyzing these same samples to which known concentrations of mercury standard solution were pipetted (table 4). It is evident from table 4 that no appreciable mercury was lost during the digestion process. Single extraction efficiency was greater than 97 percent.

Table 2. Mercury analysis of six rock and soil samples.

Sample No.	Description <sup>1</sup>	Mercury, in parts per million	
		Vaughn-McCarthy	Proposed Method (mean value)
1	Ferruginous limestone	7.5	1.55
2	Gossan	37.0	16.64
3	Phonolite	2.1	0.77
4	Gossan	0.25	1.36
5	Soil	26.0	10.75
6	Soil	0.52	0.52

<sup>1</sup>Sample nos. 5 and 6 contain 10 and 17 percent organic matter, respectively.

Table 3. Mercury analysis of six rock and soil samples showing replicate analyses, mean values and standard deviations.

Sample No.	Description	Mercury, in parts per million	Mean Value <sup>1</sup>	Standard Deviation
1	Ferruginous limestone	1.50, 1.55, 1.55, 1.55, 1.60	1.55	0.035
2	Gossan	17.00, 16.50, 16.90, 16.25, 16.55	16.64	0.304
3	Phonolite	0.72, 0.84, 0.83, 0.70	0.77	0.063
4	Gossan	1.40, 1.45, 1.25	1.36	0.085
5	Soil	10.80, 10.75, 11.20, 10.45, 10.55	10.75	0.130
6	Soil	0.49, 0.53, 0.50, 0.52, 0.55	0.52	0.021

<sup>1</sup>Values reported in table 2.

Table 4. Results obtained on standard samples.

Sample No.	Mercury, in parts per million	Mercury found
	Mercury present (table 2 values plus 10 $\mu$ g)	
1	11.55	10.91
2	26.64	26.80
3	10.77	10.20
4	11.36	10.38
5	20.75	19.35
6	10.52	9.80

In addition to comparing results with the Vaughn-McCarthy method, sample determinations were compared with other independent laboratories.

Fifteen Arizona soil samples were analyzed for mercury and results compared with determinations performed by independent lab #1 (table 5). The latter were obtained using the Lemaire SV mercury detector. Discrepancies between the two methods can be attributed in part to different sample mesh fractions; the -35 mesh fraction was used with the Lemaire instrument. However, sample organic matter is most likely responsible for the larger discrepancies. The problems encountered by single beam instruments of the Lemaire type with organic rich samples are well documented (Azzaria and Webber, 1969). With single beam instruments, higher than actual values may result. Samples nos. 2, 7 and 11 contain about 10 per cent by weight organic matter; sample no. 15 is very low in organics.

Similarly, determinations were performed on 13 soils of varying organic content provided by Geologic Research Unit, RST Technical Services Limited of Kalulushi, Zambia, Africa. Results were compared with determinations performed on these samples by two independent laboratories (table 6). The Lemaire SV mercury detector and an unspecified technique were used in the determinations. The results from all three methods are compared graphically in figure 4. Agreement exists between independent lab #2 and the proposed method; anomalies

Table 5. Mercury analysis of some Arizona soil samples.

Sample No. <sup>1,2</sup>	Mercury, in parts per billion	
	Lemaire SV Detector (-35 mesh fraction)	Proposed Method (-100 mesh fraction)
1	290, 226, 155	200, 220
2	200, 175	60, 70
3	16	50, 50
4	57	50, 50
5	29	60, 60
6	64	50, 50
7	120, 124	50, 50
8	64, 74	50, 50
9	82, 86	50, 60
10	73, 72	100, 90
11	130, 172	70, 70
12	57	50, 50
13	29	50, 60
14	64	50, 50
15	246, 240	400, 410

<sup>1</sup> Sample nos 12, 13 and 14 are duplicates of sample nos. 4, 5 and 6.

<sup>2</sup> Sample nos. 2, 7 and 11 contain about 10 percent organic matter.

Table 6. Mercury analysis of some soil samples of varying organic content.

Sample No.	Description <sup>1</sup>	Mercury, in parts per billion		
		Lab #1 (Lemaire SV)	Lab #2 (unspecified)	Proposed Method
1	Argillite, A <sub>1</sub> soil horizon	119	79	70
2	Argillite, A <sub>2</sub> soil horizon	140	250	150
3	Argillite, C soil horizon	143	56	50
4	Argillite, D soil horizon	-	37	50
5	Argillite, Rubble soil horizon	125	119	90
6	Dolomite, A <sub>1</sub> soil horizon	107	77	50
7	Dolomite, A <sub>2</sub> soil horizon	209	220	160
8	Dolomite, C soil horizon	89	30	50
9	Dolomite, D soil horizon	89	28	50
10	Dolomite, Rubble soil horizon	116	93	170
11	Argillite, D soil horizon	119	28	70
12	Argillite, ore horizon	118	709	360
13	Argillite, ore horizon	124	158	90

<sup>1</sup>Sample nos. 12 and 13 are low in organic matter.

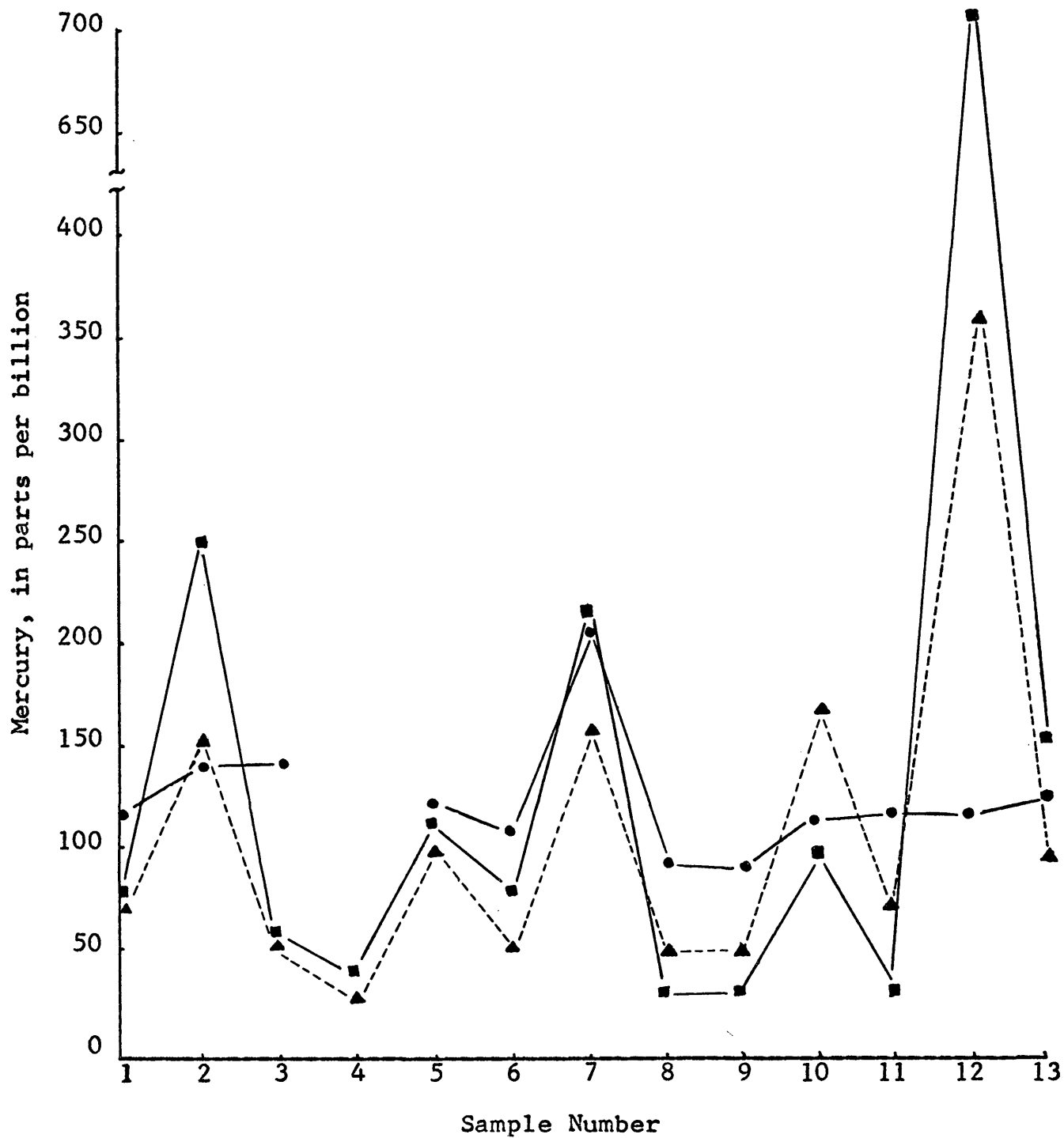


Figure 4. Mercury analysis of soil samples of varying organic content using a Lemaire SV mercury detector (-●-), an unspecified technique (-■-) and the proposed method (-▲-).

appear to coincide well. Where discrepancies do exist, organics may be responsible. Values obtained with the Lemaire instrument miss the anomalies altogether.

#### Analysis of Mercury in Vegetation

A number of analytical procedures are available for determining heavy metals in plants (Reichen and Lakin, 1949; Reichen and Ward, 1951; Ward and McHugh, 1964). Chemical analysis of systematically sampled vegetation for traces of ore metals has been shown to be a valuable tool for geochemical exploration (Webb and Millman, 1951; Marmo, 1953; Bloss and Steiner, 1960). Moreover, detection of toxic amounts of metals as contaminants in natural products is often necessary. Detection of microgram and nanogram quantities of mercury contamination in grain crops has to date been primarily done with neutron activation (Livingston, Smith and Stojanovic, 1967).

With only a slight modification of the digestion procedure, microgram and nanogram quantities of mercury in vegetation can be detected with this proposed technique.

A two gram sample of organic material is weighed and transferred into a culture tube (20- x 200-mm). Ten ml of concentrated nitric acid is added to the culture tube and the sample is digested carefully on a hot plate (200°-230°C) until less than two ml of solution remain. By this time, all the solid organic matter should be in solution. Sample solutions are then cooled, after which two ml of concentrated

perchloric acid are added and then the mixture again digested on the hot plate for one hour.

After cooling, the sample is diluted with demineralized water to a total volume of 30 ml (pH 0.1). Five ml of dithizone solution are added to the sample solution and the tube shaken for 30 seconds to extract the mercury into the organic layer.

A blank is prepared from each sample and run before a sample analysis. An equal weight of sample is similarly digested, cooled and diluted with demineralized water. Five ml of pure methyl iso-butyl ketone solvent are added to the sample solution and the tube shaken for 30 seconds. This organic layer is aspirated to adjust the instrumental zero prior to analyzing for mercury in the sample.

A detection limit of 25 parts per billion in a two gram sample can be achieved; with increased sample size even lower detection limits are possible.

Eight samples of grain seed believed to be contaminated by mercury derivative pesticides were analyzed for trace mercury. The analytical results for the dry seeds check well with neutron activation analysis done on duplicate samples by Isotope Techniques, Inc., Stockholm, Sweden (table 7).

Table 7. Mercury analysis of grain seed samples.

Sample No.	Description	Mercury, in parts per billion	Neutron Activation <sup>1</sup> Proposed Method
1	Whole seeds	21 ± 8	35
2	Ground seeds	21 ± 8	25
3	Whole seeds	29 ± 22	65
4	Ground seeds	29 ± 22	60
5	Whole seeds	53	95
6	Ground seeds	73	85
7	Whole seeds	85	80
8	Ground seeds	97	75

<sup>1</sup>Standard deviation unavailable for sample nos. 5, 6, 7 and 8.

### CONCLUSIONS

The dithizone - methyl iso-butyl ketone extraction system can be utilized with atomic absorption spectrophotometric determinations of microgram and nanogram concentrations of mercury in natural samples. The extraction procedure has two advantages. By analyzing the mercury in an organic solvent rather than in an aqueous medium, eight-fold signal enhancement is achieved. This permits lower detection limits to be realized. Similarly, extraction of mercury as the dithizonate separates the cation from possible interfering ions left behind in the aqueous phase.

Silver, gold and palladium, also chelated and extracted by dithizone from dilute acid solution, were investigated along with mercury. Using the dithizone - methyl iso-butyl ketone extraction procedure and atomic absorption spectrophotometry, calibration curves for silver, gold and palladium were determined. From these calibration curves lower limits of detection for silver, gold and palladium were found to be  $0.005 \mu\text{g}$ ,  $0.025 \mu\text{g}$  and  $0.005 \mu\text{g}$ , respectively.

Unfortunately, the analysis of natural samples for silver, gold or palladium by this method is difficult. Experimental evidence suggests that the silver, gold and palladium dithizonates are considerably less stable in methyl

iso-butyl ketone than the mercury dithizonate. Palladium appears to form a stronger dithizonate than either silver or gold. The Ag (I) and Au (III) species probably form chelate systems with one or three molecules of dithizone, whereas Hg (II) and Pd (II) involve dithizone as a bidentate chelating agent. This instability of the silver, gold and palladium dithizonates makes extraction efficiencies for the three chelates dependent upon the presence or absence of foreign cations and anions.

Neither copper, gold, platinum nor silver will interfere in the mercury determination even at concentrations of 2,000 parts per million each, in the sample. Palladium shows no interferences below concentrations of 250 parts per million.

Organic matter, that generally causes severe interferences in other instrumental techniques, is destroyed by the hot nitric-perchloric acid digestion and does not interfere in the technique. Gorsuch (1959) suggests that some mercury may be lost during hot nitric-perchloric digestion of organic-rich samples and attributes this to the formation of volatile mercury compounds or complexes during digestion. Loss of appreciable amounts of perchloric acid fumes during sample digestion will result in lower values for mercury. For this reason, tall (20- x 200-mm) culture tubes are recommended in the digestion procedure. At the specified digestion temperature, perchloric acid fumes condense on the upper neck of the culture

tube. As indicated in table 4, little if any mercury loss will occur during digestion. Likewise, little if any mercury was lost during the intense digestion of the dry seeds, wholly organic in composition. The analytical results for the seeds check well with neutron activation analysis (table 7).

With access to an atomic absorption spectrophotometer, the proposed method is simple, convenient, inexpensive and rapid for the determination of mercury in the parts per million and parts per billion range in rock and soil samples. Moreover, this procedure can be applied successfully to the detection of trace amounts of mercury in vegetation.

APPENDIX

Some of the cation interferences that can be expected with direct determination of mercuric ions in aqueous - acid solution by atomic absorption are shown in table 8. Each test solution was prepared by pipetting 2 ml concentrated perchloric acid, 30  $\mu$ g mercuric ion and 3,000  $\mu$ g of interfering cation. Since test solutions were diluted with demineralized water to a total volume of 30 ml, the solutions were 1 ppm in mercury and 100 ppm in interfering cation. Such interferences are eliminated by the proposed method.

Optimum pH conditions for the chelation and extraction of Ag (I), Au (III), Hg (II) and Pd (II) as the dithizonates into MIBK are shown in table 9.

Table 8. Effect of various cations on the direct determination of mercury in aqueous - acid solution by atomic absorption.<sup>1</sup>

Sample No.	Interfering Cation	Percent Absorption	Mercury determined in aqueous media by proposed method	Mercury determined by proposed method
1	none	1.02	25.38	25.38
2	Li	4.08	25.52	25.52
3	Na	1.10	25.50	25.50
4	K	1.30	25.46	25.46
5	Mg	0.40	25.34	25.34
6	Ca	1.04	25.54	25.54
7	Cu	1.06	25.40	25.40
8	Pb	1.24	25.38	25.38
9	Zn	1.38	25.40	25.40

<sup>1</sup>One part per million mercury in the presence of 100 parts per million second element.

Table 9. Extraction efficiency of silver dithizonate, gold dithizonate, mercury dithizonate and palladium dithizonate as a function of pH.

pH	Percentage of metal extracted in initial 5 ml extraction			
	Silver (I)	Gold (III)	Mercury (II)	Palladium (II)
-0.50	--	--	0.0	--
-0.36	40.3	31.3	--	45.1
-0.08	75.3	88.8	99.6	72.4
0.10	92.7	93.8	99.9	83.9
0.22	98.3	94.8	99.6	91.5
0.31	--	98.5	--	95.6
0.40	--	--	88.0	98.2
0.70	--	--	84.5	--
1.00	--	--	80.5	--
1.40	--	--	72.7	--

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