UNITED STATES, GEOLOGICAL SURVEY.

Trace and Investigations Report

TEI-236

A THEORETICAL TREATMENT OF THE ABSORPTION CHARACTERISTICS OF THE DITHIZONE MIXED-COLOR SYSTEM

By
Robert G. Milkay

May 1952

CHEMISTRY

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CONTENTS

ABSTRACT

The equation of the standard curve used in the colorimetric determination of trace amounts of metals by means of dithizone extraction is developed, and a further expression is derived which defines the slope of the standard curve.

These equations are used to show the relative effect and importance of the different factors that enter into the construction of the curve. The equations are further utilized to calculate a numerical value for the slope of the standard curve, when lead is the metal determined. When this figure is compared with the slopes of curves

*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

determined experimentally, the close correlation of values shows
that the interfering factors which may be present are not of
sufficient significance to affect the analysis.

INTRODUCTION

It is common procedure to determine trace amounts of lead
by means of dithizone extraction.

The solution containing the lead is adjusted to a pH of 9
to 10.5, and various complexing agents are added to prevent the
extraction of other reacting elements that may be present. The
lead is then extracted with a dilute solution of dithizone in
chloroform, and the optical density of the dithizone solution is
determined with a spectrophotometer at an appropriate wavelength
of light.

The lead content of the solution is determined from a standard
curve, expressed in terms of the optical density of solution versus
micrograms of lead.

The question arises whether the standard curve has a constant
or a varying slope. Conformance to Beer's Law in one part of the
curve (dilute solutions) does not insure a straight-line function
throughout the range of the curve.

Once the standard curve has been established, the analyst will
discover that it does not necessarily remain applicable for any
appreciable length of time. This will be a matter of some importance,
as the standard curve is the basis of the analysis.

The explanation for these and for other characteristics
of the curve lies in an analysis of the factors that enter into
the derivation of the standard curve.

This work was done on behalf of the U. S. Atomic Energy Commission.

DISCUSSION

First of all, it is necessary to define some of the factors
which determine the standard curve.

These are:

1. The presence of mixed-color system. The density of
the dithizone solution is the result of two absorbing systems--
the absorption due to the lead-dithizonate formed in the extraction
and in addition the absorption due to the dithizone left in the
solution after the reaction.

2. The characteristics of the dithizone solution used.

a. Changes in concentration from one dithizone solution
to the next. 'It is difficult to prepare dithizone solutions which
are exact duplicates in concentration.

b. Degree of instability of the solution especially
in sunlight and warm weather.

c. The presence of impurities in the dithizone used.

3. Contamination from apparatus, reagents, and from the
atmosphere.

The questions then arise: To what degree does a change in
any of these factors affect the usability of the curve? If these
factors are susceptible to appreciable change, will it be necessary

to make almost day-to-day rechecks to be sure that the curve
still applies?

If one analyzes the system mathematically, the resulting
equations make for an understanding of the disturbances introduced
by these factors and of their relative importance.

DERIVATION

Assume a divalent metal in aqueous solution, extracted with
a dilute solution of dithizone in chloroform.

$$Me^{++} + 2 Dz \rightarrow Me (Dz)_2 + 2H^+$$
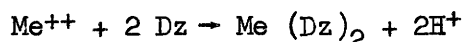
The optical density of the resulting organic solution =
density of dithizone present + density of metal-dithizonate formed.

Assuming conformance to Beer's Law:

Density $= k_1 c_1 l + k_2 c_2 l$, where subscript 1 refers to
dithizone, and subscript 2 refers to dithizonate.

Let V = unit weight metal / ml organic solution.

Let $\underline{C}$ = original concentration dithizone solution, mg per ml.

Add 1 unit weight of metal:

Dithizone equivalent of metal $= \underline{K}_1 V$

Dithizonate equivalent of metal $= \underline{K}_2 V$

Density of solution = density dithizone + density dithizonate.

$$= k_1 c_1 L + k_2 c_2 L$$

$$= k_1 (\underline{C} - \underline{K}_1 V)L + k_2 \underline{K}_2 V L$$

Add 2 unit weights of metal:

Density of solution $= k_1 (\underline{C} - 2\underline{K}_1 V)L + 2k_2 \underline{K}_2 V L$

Add "n" unit weights of metal:

Density of solution $= k_1 (\underline{C} - n\underline{K}_1 V)L + nk_2\underline{K}_2 V L$

$$= k_1 \underline{C}L - nk_1 \underline{K}_1 V L + nk_2\underline{K}_2 V L$$

$$= nVL(k_2\underline{K}_2 - k_1\underline{K}_1) + k_1 \underline{C} L$$

which is, thus, the equation of the standard curve.

When "n" = zero units:

Density $= (0 \text{ units}) \cdot [VL(k_2\underline{K}_2 - k_1\underline{K}_1)] + k_1\underline{C} L$

$$= k_1 \underline{C} L$$

The slope of the density curve, that is, the rate of change

of the density with change in unit weights of metal, will be the

differential of the density expression:

slope $= d(\text{density}) / dn$

$$= V L(k_2\underline{K}_2 - k_1 \underline{K}_1)$$

INTERPRETATION

The curve of density versus weight of metal extracted is a

straight line, as the slope is a constant and the original density,

or concentration of dithizone, $\underline{C}$, appears only in the expression which

defines the zero intercept. Then the concentration of the dithizone

solution used in the extraction will have no effect on the slope or

shape of the standard curve. Changes in day-to-day concentration of

the solution will merely shift vertically the position of the curve.

The same effect will obtain from the presence in the dithizone, in

constant amount, of elements that react with dithizone under the same

conditions and thus contribute to the density.

In practice a blank can be run with each batch of samples, and the density of the blank sample can be used to determine the zero intercept of the curve. From this zero intercept the line with the standard slope (once the slope has been determined) can then be drawn, and the values for the samples can be read directly.

Curves obtained at different intervals of time will all be parallel lines with varying zero intercepts. The controlling factor in determining the standard slope is in the optics of the spectrophotometer. An occasional check point may be made to ascertain the consistency of the spectrophotometer. Other than that, the analyst at his own discretion may safely eliminate the time-consuming repetitious rechecks of the standard curve that are usually recommended.

CALCULATION OF SLOPE

Proceeding from the above theoretical expression of the standard curve, it is possible to calculate numerical values for the terms, and derive an actual theoretical value for the slope of the curve. Let lead be the metal to be extracted, and assume that the keto-tautomerism of the dithizonate is formed:

K_1 = dithizone equivalent of lead

Equivalent weight of lead = $(207.2)/2$

Equivalent weight of dithizone = 256.06

$$K_1 = \left[\frac{256.06}{(207.2)/2} \right] \cdot \text{(weight Pb)}$$

$$= \left[\frac{512.12}{207.2} \right] \cdot \text{(Pb)}$$

$\underline{K_2}$ = lead dithizonate equivalent of lead

Equivalent weight of lead = 207.2

Equivalent weight of lead dithizonate = 717.3

$$\underline{K_2} = \left[\frac{717.3}{207.2}\right] \cdot (Pb)$$

Let V = the unit weight of metal = (1 microgram Pb)/(15 ml solution)

$$V = \frac{0.001}{15} \qquad (\text{mg Pb}) / (\text{ml dithizone})$$

L = length of light path in solution.

k_1 = extinction coefficient of dithizone. To obtain this constant, a dithizone solution in chloroform was prepared from purified dithizone, at a concentration of 8 mg per liter. The density was determined at a wavelength of 520 mμ and slit width of 0.03 mm, with a light path of 1 cm (corex cell). The density was 0.194.

Therefore, $0.194 = k_1 c_1 L$

$$0.194 = k_1 (8/1000) (1)$$

$$k_1 = \frac{194}{8} = 24.25 \text{ cm} / \text{mg}$$

k_2 = extinction coefficient of lead dithizonate. To obtain this coefficient, 20 ml of a solution which contained 1 mg Pb per ml was adjusted to a pH of approximately 9.5, and shaken with 15 ml of the solution of dithizone. The density of the red dithizonate solution at a wavelength of 520 mμ and slit width of 0.03 mm was determined to be 0.946.

Therefore, $0.946 = k_2 c_2 L$

$$0.946 = k_2 \left[\left(\frac{8}{1000}\right) \left(\frac{717.3}{512.12}\right) (1)\right]$$

$$k_2 = \left(\frac{946}{8}\right) \left(\frac{512.12}{717.3}\right) = 84.43 \text{ cm} / \text{mg}$$

Slope of standard curve $= V L (k_2 K_2 - k_1 K_1)$

Standard slope $= \left(\dfrac{0.001}{15}\right) (1) \left[(84.43) \left(\dfrac{717.3}{207.2}\right) - (24.25) \left(\dfrac{512.1}{207.2}\right)\right]$

$= \dfrac{0.001}{15} \left[(292.13) - (59.89)\right]$

$= \dfrac{0.001}{15} (232.24) = 0.0155$ units density / micrograms Pb

The slopes of some of the standard curves determined experimentally were 0.0155, 0.0155, 0.0159, 0.0159, 0.0163. The average of the slopes of eight standard curves, derived from points from 0 to 20 micrograms lead and determined during the course of several months' analyses, was 0.0162 units density / microgram lead. These lead analyses were made as part of a study of carnotite ores for purposes of age determination of minerals. [1, 2] The difference between the experimental and theoretical values is 4.3 percent of the experimental -- a value which is within the realm of accuracy of such colorimetric analyses.

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[1] Milkey, R. G., The methods of analysis used in the treatment of Colorado Plateau carnotite for age studies: U. S. Geol. Survey Trace Elements Investigations Rept. (in preparation).

[2] Stieff, L. R., Stern, T. W., and Milkey, R. G., A preliminary determination of the age of some Colorado Plateau uranium ores by the lead-uranium and lead-lead methods: U. S. Geol. Survey Trace Elements Investigations Rept. (in preparation).

In the derivation of the value of the standard slope, it was assumed that the lead dithizonate equivalent weight was 717.3, which corresponds to the keto-form of the compound
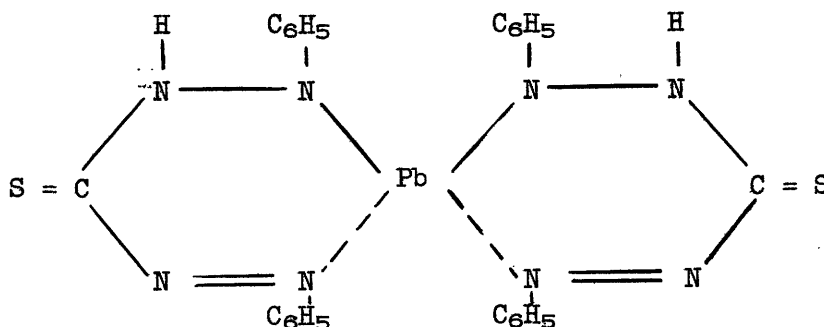
rather than a weight of 561.39, which corresponds to the enol-form:
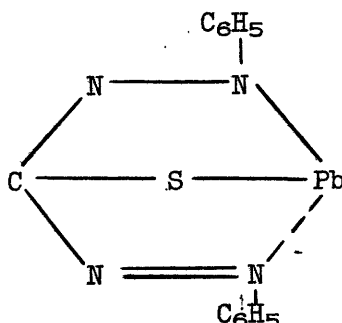
The results substantiate this initial assumption.

The results also indicate neither a change in the partition coefficient of dithizone between the chloroform and aqueous phases, with the variation of total lead extracted, nor the incidence of molecule and ion association within the solution has enough of an effect to alter significantly the shape of the standard curve. The system follows Beer's Law over its entire length.

It is thus possible, when the metal-dithizonate to be formed is lead, to calculate a check for the experimentally determined standard curve. This calculated curve is most helpful when the range of lead to be determined is 1 to 2 micrograms or less; for with such dilute solutions contamination of the sample is particularly troublesome, and the points determining the curve could assume random positions. When the analyst is determining a standard curve for use in such lead determinations, he may, by reference to the calculated curve, make a judiciuos selection of the points which represent samples that have obviously been contaminated during the analysis.

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