LTD 45-57
December 14, 1945

DETERMINATION OF LEAD BY DITHIZONE

A Critical Comparison of the Methods Described in LTD 42-5 and DSM 44-188

PURPOSE

(1) To evaluate certain factors in the "mixed-color" method for lead given in LTD 42-5.

(2) To compare this method with the "one-color" method described in DSM 44-188.

(3) To check the sulfite reduction method, given in DSM 45-39, for the removal of iodine from the solutions obtained in the determination of TEL in air.

SUMMARY

The two methods have been compared with respect to the effects of concentration and pH of the lead solution, concentration and age of the reagent, presence of phosphate, and stability of the final solution.

The methods are of comparable sensitivity and, with proper control of experimental conditions, appear to be equal in accuracy. However, it is believed that further, special experimental tests are needed to demonstrate unequivocally the quantitative recovery of lead from very dilute solutions in the one- color method.

Contrary to the results given in DSM 44-188 it was found that the solutions obtained by the one-color method were relatively unstable on standing, so that careful timing of the analysis was required. This point should receive further investigation before the method can be recommended for general use. At present, for laboratory use, the preferred method is that of LTD 42-5, modified to avoid a small interference from phosphate in the second extraction.

The sulfite reduction of iodine solutions is satisfactory, if the organic lead iodides are first decomposed by heating. The resulting solution can be analyzed for lead by the mixed-color method.

INTRODUCTION

There are two major procedures for the use of dithizone (diphenylthiocarbazone) for the determination of lead. These have been designated as the "one-color" and the "mixed-color" methods. Both involve the extraction of the lead ion from an alkaline solution (pH 8.5 to 11) with an excess of dithizone in chloroform, and observation of the colored lead dithizonate in the chloroform solution.

The procedure used in this Laboratory (LTD 42-5) for the determination of small amounts of lead by dithizone, is based on the well known and generally accepted mixed-color method. Briefly, the lead in 1% nitric acid solution is treated with citric acid, potassium cyanide, and ammonium hydroxide to bring the solution to pH 9.5. The lead is then extracted with a chloroform solution of dithizone. A portion of the excess dithizone dissolves in the ammoniacal solution, but sufficient remains in the chloroform to give it a green to violet color. However, with a spectrophotometer, the red color of the lead dithizonate in the chloroform solution is readily determined.

Recently the Baton Rouge Development Section Laboratory (DSM 44-188) proposed a modification of the original one-color method. Instead of extracting the lead at a pH of about 9 and then removing the excess dithizone by shaking with dilute ammonia, as in other one-color methods, the Baton Rouge method carries out the extraction at a pH of 1.2. At this pH, the excess dithizone is almost completely extracted b the aqueous solution, leaving only the red lead dithizonate in the chloroform. It was known that lead dithizonate is also extracted in part from the chloroform by aqueous solutions at pH 11 to 12, but in the present method, the large excess of free dithizone in the solution apparently prevents this.

Either dithizone procedure is far from ideal. Several dependent equilibria are involved:

1. Reversible reaction of lead with dithizone.

2. Distribution of lead dithizonate between water and chloroform.

3. Distribution of dithizone between water and chloroform.

4. Shifting of these equilibria with variations in pH.

Systems involving such equilibria must be carefully standardized before they can be used for quantitative analysis. Likewise, one must recognize that in the use of such systems one cannot predict the effect of any variable but must specifically verify every conclusion by experiment.

When Clifford and Wichmann[1] studied the one-color method of Winters, et. al.[3], they stated: "Analysts using one-color methods find themselves in a dilemma. If they do not remove all the unbound dithizone, their results are high, and if they take meticulous care to remove it, they lose lead in the process .... The greatest accuracy of one-color methods is about 0.001 mg."

For this reason, and because of the wide availability of spectrophotometric equipment, the mixed-color method has become greatly recommended. In this method, the presence of some excess reagent is not objectionable. The preparation of the blank for lead in the reagents, under the same conditions as the samples, provides an accurate correction of any errors thus introduced. Variable slit-width instruments such as the Beckman quartz spectrophotometer or the Cenco Spectrophotelometer permit such compensation without decreasing the range of the method. Fortunately, the lead dithizonate exhibits its maximum absorption at the wave length where the dithizone itself shows minimum absorption. Thus, for photometric measurement, the presence of the green color of the dithizone reagent, even in excess, is of no disadvantage. For visual comparison the change in hue seems to be even more easily distinguishable than a change in color intensity. With an appropriate choice of reagent concentration Clifford and Wichmann[1] could distinguish visually ten steps between 0 and 1 microgram of lead.

Nevertheless, the one-color method proposed in DSM 44-188 offers a new approach to the problem, which may have advantages for certain uses. It seemed, therefore, desirable to make an independent check of this method.

EXPERIMENTAL

Effect of Lead Concentration. In the presence of an excess of reagent, both methods obey Beer's Law, as shown in Fig. 1. These standard series were run under the conditions described in DSM 44-188 and LTD 42-5. The procedure from LTD 42-5 was changed slightly to eliminate phosphate interference, which is discussed in detail in another part of this report. The data indicate the methods are comparable with respect to sensitivity. Using 1-cm. cells, from 0.004 to 0.082 mg. Pb can be determined using the maximum useful range of the spectrophotometer. This range is from 10% to 90% transmittancy, as shown in Table I. The decreased accuracy at high and low transmittancies results from the logarithmic relationship between color intensity and concentration of colored substance. It will be noted that in a careful study of the effect of a variable in a colored system it is desirable to limit transmission readings between 20% and 60%.

TABLE I - Variation in Errors over Transmittancy Range

Transmittancy	Concentration mg.Pb	Absolute Error for 1% Transmittancy mg.Pb	% Error
95	0.002	0.00015	7.50%
90	.004	.00025	6.25%
80	.008	.00040	5.00%
70	.0125	.00055	4.30%
60	.018	.00055	3.00%
50	.0245	.00070	2.80%
40	.0325	.00090	2.76%
30	.043	.00110	2.50%
20	.058	.00175	3.00%
10	.082	.00400	4.90%
5	.117	.00800	6.80%

Because of the ease of extraction of the lead salt and its extremely favorable distribution between chloroform and water, both methods are extremely flexible, with respect to sensitivity. The applicable range of lead concentration can be extended considerably in both directions by varying the volume and concentration of the reagent solution. For example, Stenger[2] has applied the method to magnesium-base alloys, using such a combination of these variables that the range for 1 cm. cells is 0.002 to 0.014 mg. Pb. However, such changes in procedure should be completely verified experimentally.

Effect of pH. In either dithizone method for lead, the pH is the critical variable. In fact the only essential difference between the mixed-color method and the one-color method is in the pH used. In both methods the ease of control is of prime importance and the methods are comparable in this respect. Both systems are highly buffered by ammonium and cyanide ions and only a rough measurement of the various solutions used is required to furnish the desired pH.

Chloroform solutions, containing approximately 0.025 mg. and 0.075 mg. lead respectively, were prepared to determine the solubility of the lead dithizonate in the aqueous phase when extracted in accordance with the method described in DSM 44-188. Instead of determining the lead dithizonate photometrically after the first extraction as required in the method, as many as three repeat extractions with fresh aqueous solution, at pH 11.4, were performed on individual samples. The results of these tests given in Table II show that the lead dithizonate distributes between the chloroform and the aqueous phases, when no excess dithizone is present.

TABLE II - Solubility of Lead Dithizonate at pH 11.4

Additional Extractions	T*510	mg. Pb	Pb mg. Loss
0	52.5	0.0255	---
1	59	.0210	0.0045
2	67	.0160	.0095
3	77	.0105	.0150
0	10.8	.080	---
1	16.0	.065	.015
2	20.5	.0565	.0235
3	27.0	.047	.033

* Transmittancy

These conditions are not applicable to the method described in DSM 44-188. The first extracting solution contained everything in the proper concentration, but, during the additional extractions, there was only a slight excess of dithizone. In an effort to determine whether any loss occurred in the presence of excess dithizone at this pH, another series was prepared and extractions were carried out with 50 ml. portions of the water layer obtained from running a series of blanks. In this way a solution was prepared for additional extractions which corresponded to the usual extracting solution. The results of these tests are given in Table III.

TABLE III - Lead Loss of pH 11.4 in Presence of Excess Dithizone

Additional Extractions	T 510	mg. Pb	Pb mg. Loss
0	53	0.0225	---
1	50	.0250	-0.0025
2	52	.0230	-0.0005

A repetition of this series of tests gave the same results, including the same slight increase in apparent lead for the sample which received only one additional extraction. Recognizing that the solubility of lead dithizonate is small under these conditions and that there is sufficient lead in the water and reagents to cause an appreciable blank, further experiments seemed useless for our purpose. However, it is suggested that this solubility be determined by some independent method on solutions which have been carefully freed of lead. We would likewise suggest that any such experiments should include more than one concentration of lead, expecially one in the concentration range requiring the use of 5-cm. cells.

Stability of Lead Dithizonate. In an attempt to compare the two methods for low concentration of lead, using 5-cm. cells, a standard series of solution containing between 0 and 0.020 mg. Pb was prepared by each method. Erratic results which did not fall about a straight line were obtained by the DSM 44-188 method. After standing a short time, one of the very weak solutions changed from pink to green. It was suspected that under ordinary laboratory conditions these solutions were sufficiently unstable to require a careful control of time. To determine the effect of time, standard lead series for 5-cm. cells and 1-cm. cells were prepared and timed carefully. A straight line was obtained in each case. Readings were taken on some of the solutions after they stood in the dark, at room temperature, and in the transmission cells. The data for 5-cm. cells are given in Table IV and for 1-cm. cells in Table V.

TABLE IV - Stability Studies Using 5-cm. Cells

DSM 44-188 Method						LTD 42-5 Method					
5 min.		10 min.		105 min.		5 min.		10 min.		40 min.	
T510	mg.Pb	T510	mg.Pb	T510	mg.Pb	T510	mg.Pb	T510	mg.Pb	T510	mg.Pb
92.5	0.001	95	0.0007	--	--	92	0.001	92.2	0.0009	--	--
78.0	.0025	85	.0015	87.0	0.0012	77.8	.0025	77.5	.0024	77.6	0.0024
57.0	.005	63.5	.0040	--	--	55.8	.005	56	.0051	--	--
40.5	.0075	44.0	.0068	56.2	.0048	42.9	.0075	--	--	43.2	.0076
29.9	.010	33.1	.0093	44.0	.0069	33.1	.010	--	--	33.1	.010

* Used to prepare Standard Curve

TABLE V - Stability Studies Using 1-cm. Cells

5 min.		60 min.		160 min.	
T510	mg.Pb	T510	mg.Pb	T510	mg.Pb
80.2	0.010	83	0.0065	--	--
61.5	.020	63.5	.0160	--	--
35.7	.040	37.8	.0345	38.0	0.0345
27.5	.050	29.6	.0435	--	--
20.8	.060	22.2	.0535	--	--

It will be noted that the system prepared according to LTD 42-5 is stable and that of DSM 44-188 is unstable. This instability decreases with age and decreases with an increase in the concentration lead.

Effect of Reagent Concentration. In order to determine the effect of reagent concentration, a standard curve was prepared each time a new 30-mg./l. solution of dithizone was prepared and these curves were compared with a standard curve for 20-mg./l. solution. The results of these tests are shown in Fig. 2. It will be noted that there is no significant variation for the 30-mg./l. solutions which were prepared from different batches of chloroform and from dithizone obtained from different sources. At lower concentrations of lead no error is evident due to a decrease of one-third in the concentration of reagent. There is a slight deviation at high concentration, near the useable limit of the method. This is in the expected direction.

Effect of Age of Reagent. Dithizone is oxidized to diphenylthiocarbodiazone. This is a yellow-brown substance, soluble in chloroform and insoluble in dilute acid or alkali. It shows significant absorption at 510 mμ. For this reason the blank will change with the age of the reagent and must be determined daily. The necessity for such a determination is important in both one-color and mixed-color methods.

A 30-mg./l. dithizone solution was allowed to stand at room temperature for several days. A portion of standard lead was analyzed by the mixed-color method described in LTD 42-5 using this solution and by the method described in DSM 44-188 using another portion of this solution diluted to 20 mg./l. with chloroform.

The results of these analyses compared with a similar series made with fresh reagent are given in Table VI from which it will be noted that low results are likely to be obtained by either method if a decomposed reagent is used.

TABLE VI - Effect of Age of Reagent

Method	mg. Pb	T 510		
		Old Reagent	Standard Curve	New Reagent
LTD 42-5	0.025	58.0	54.0	53.5
DSM 44-188	.025	56.2	49.5	49.1

Effect of Phosphate. It is an accepted fact that, in the absence of ammonium citrate, phosphate will interfere with the determination of lead by the mixed color dithizone method. In our earlier studies, the presence of phosphate impurity in the potassium cyanide was not recognized. In Fig. 2, curves for several different dithizone relations are shown using the same stock of potassium cyanide. These were prepared following the directions given in LTD 42-5. In the original procedure, the lead was separated from possible interfering substances in a first series of extractions. Then the lead dithizonate

was decomposed by dilute nitric acid and this solution adjusted to pH 9.5, without the addition of citric acid since the solution was practically free of all possible interfering subatances. Potassium cyanide was, however, added to this solution. Because of the possible interference of the small amount of phosphate present in the cyanide, and since citrate prevented phosphate interference in the first extraction, its addition to this solution was tried. We found that the addition of 5 ml. of 5% ammonium citrate solution would eliminate the interference of up to 250 mg. of phosphate.

It is recommended therefore, that the method of LTD 42-5 should be changed to include the addition of 5 ml. of a 5% solution of ammonium citrate to the nitric acid solution of the sample before the addition of solution B (described in LTD 42-5); or 12.5 g. ammonium citrate may be added to 1 liter of solution B.

Application to Determination of TEL in Air. DSM 45-39 recommended the elimination of the long heat dehydration procedure and the substitution of sulfite reduction. The final lead determination could be made in two ways:

1. The iodine solution is heated to 100° C. and this temperature is maintained for one minute. After cooling, it is added to a sulfite solution which reduces the iodine. Lead is determined by the procedure recommended in DSM 44-188.

2. The unheated iodine solution is added to a sulfite solution containing both cyanide and ammonia. This solution, with a pH of 11.4, is extracted with a chloroform solution of dithizone. A compound with an absorption maximum at 490 mμ remains in the chloroform. A measurement of this color permits a determination of the lead. This color is attributed to the dithizone complex of an organo-lead ion.

It is believed that the lead complex is other than the trialkyllead iodide, since synthetic triethyllead iodide is insoluble in the usual solvents (water, ammonia), is liquid above 18° C., and does not react like the other trialkyllead halides.

The application of the mixed-color method to the determination of TEL in iodine solutions was studied. It was found that the regular mixed color procedure could be applied if first the organo-lead complexes were decomposed by heating in the presence of an excess of iodine and if the excess iodine was removed with sulfite. However, the mixed color method was unsatisfactory for direct reaction of the organo-lead ions. The expected reaction took place but at least 50% of the methods sensitivity was lost due to the coincidence of the absorption maxima of the dithizone reagent and the organo-lead dithizonate.

CONCLUSIONS

The mixed-color method for determining small quantities of lead, presented in LTD 42-5, is both sensitive and accurate. It requires the use of three different solutions for the three different cell sizes in order to include very low concentrations of lead. However, the reagent concentration is not too critical and these solutions may be prepared by dilution of the stronger solutions without exact measurement. Because of the interference of the small quantities of phosphate present in the potassium cyanide, it is recommended that ammonium citrate be included in the solution for the second extraction. Otherwise, a new standard curve must be prepared for each new stock of potassium cyanide.

The one-color method recommended by the Baton Rouge Development Section laboratory compares favorably with the above method in all respects except stability. If the time of color development is not controlled, erratic results are likely to follow. This effect is more noticeable at low concentrations. In the presence of thallium and tin the one-color methods are more desirable than the mixed-color method. In our opinion, the DSM 44-188 method is an improvement over existing one-color methods. This is attributable to the presence of over 100% excess dithizone in all alkaline solutions used to remove the excess reagent from the chloroform layer.

REFERENCES

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Figure 1

Comparison of Standard Curves

Beckman Spectrophotometer
1-cm. Cells
λ = 510 mμ.

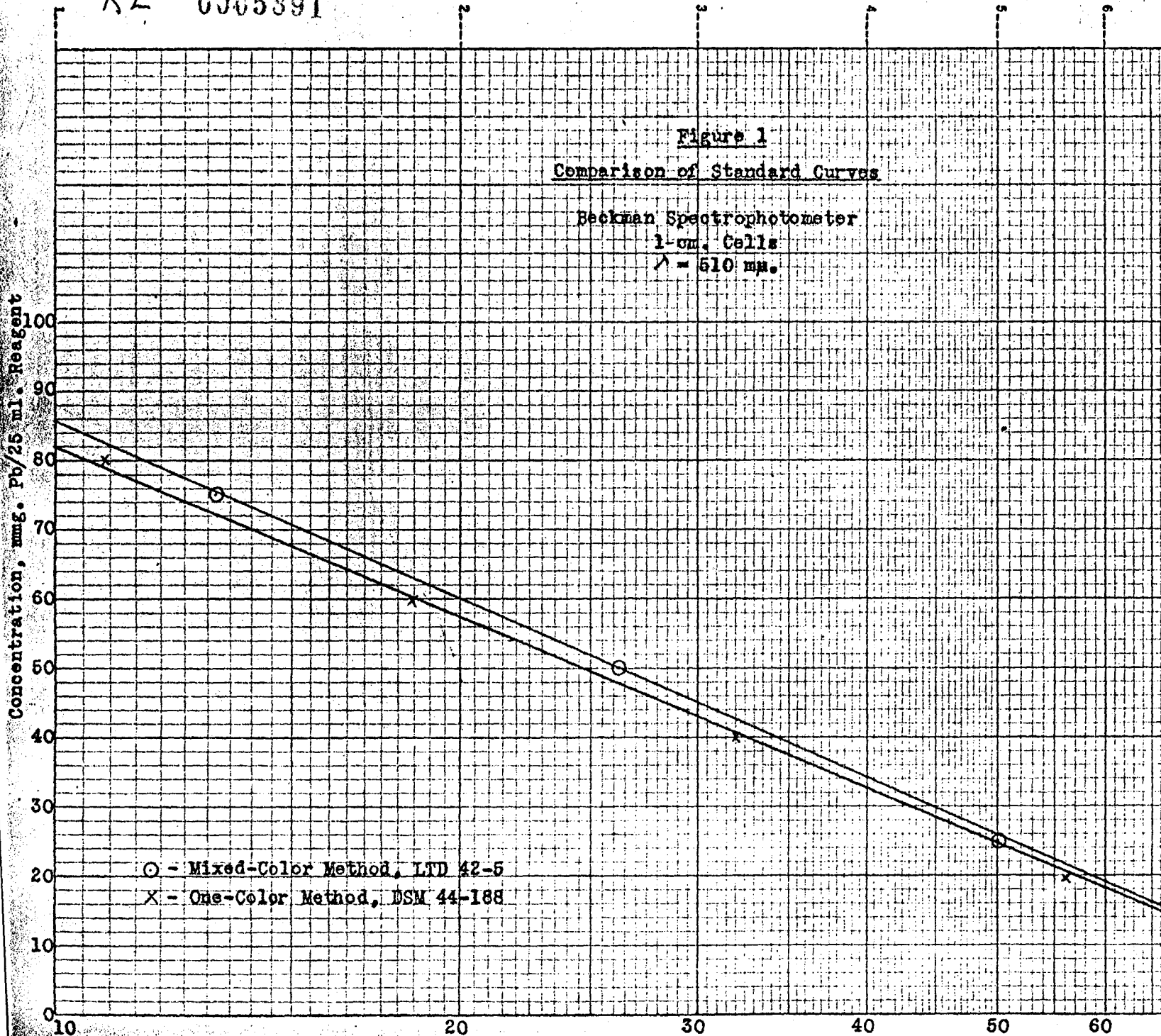

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Figure 2

Effect of Reagent Concentration

Beckman Spectrophotometer
Mixed-Color Method
1-cm. Cells
λ = 510 mμ.

Concentration, mmg. Pb/25 ml. Reagent

100
90
80
70
60
50
40
30
20
10

⊙ - 30 mg. dithizone/l.
○ - 30 mg. dithizone/l.
X - 20 mg. dithizone/l.
□ - 30 mg. Eastman dithizone/l.
△ - 30 mg. dithizone/l. with ammonium citrate present